
Determination of Heavy Metals Concentration in Soils Used for Cultivation of Vegetables in
Dorowa Mining Areas of Barkin Ladi, Plateau State, Nigeria

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ABSTRACT

Tin mining activities carried out in parts of plateau state from the beginning of this century have left behind a post mining environment scarred by numerous mine pond and uncontrolled heaps of mine. This has devastated vast portions of its land mass. Tin mining and processing constitute a source of environmental pollution due to its associated minerals which pose harmful threats in low concentration to humans and animals. The samples used for this researched work was collected from Kapang, Selebirom and Sabon Angwa all in Dorowa District mining area of Barkin Ladi, Nigeria. The experiment was designed to ascertain the concentration of some heavy metals Cr, Co, Ni, Pb, Zn, Cu and Mn. in soil used for cultivation of vegetable. The samples were analyse using EDX3600B-Energy Dispersive X-ray Fluorescence spectrometer, Jiangsu Skyray information Technology Co. Ltd. The result obtained shows the range of concentrations of heavy metals in the soil as: Cr 50.00 ± 0.02 to 16.20 ± 0.43 mg/kg, Co 902.70 ± 0.14 to 125.20 ± 0.21 mg/kg, Ni 79.20 ± 0.31 to 70.01 ± 0.12 mg/kg, Pb 67.10 ± 0.23 to 10.10 ± 0.02 mg/kg, Zn 2080.00 ± 0.67 to 1244.50 ± 0.45 mg/kg, Mn 145.40 ± 0.11 to 53.10 ± 0.01 mg/kg, Cu 65.70 ± 0.08 to 54.30 ± 0.23 mg/kg respectively. The result shows that the soil are contaminated with the heavy metals. Thus, the soil around the area will not be good for the cultivation of crops and vegetables.

Keywords: heavy metals, soils, vegetables, ED-xrf.

INTRODUCTION

Barkin Ladi Local Govt. Area of Plateau State, Nigeria, is located in the northern senatorial district of the state. It is known for the mining of Tin and columbite. Tin mining has devastated vast portions of its land mass. This is evident by the presence of mounds and ponds scattered all over the local government (Daniel *et al*, 2014). Tin mining and processing constitute a source of environmental pollution due to its associated minerals which pose harmful threats in low concentration to humans and animals (oresegun and Babalola, 1993). Soil is unconsolidated minerals and organic material found on the immediate earth surface that serves as a natural medium for plants growth and other developmental activities (Haliru *et al*, 2014). Soil is composed of mineral constituents, organic matter (humus), living organisms, air, and water, and it regulates the natural cycles of these components (Keesstra *et al* 2012 and Keesstra, *et al* 2016). Heavy metals are hazardous contaminants in food and the environment and they are non-

biodegradable having long biological half-lives (Heidarieh *et al* 2013). The implications associated with metal (embracing metalloids) contamination are of great concern, particularly in agricultural production systems (Kachenko and Singh, 2006) due to their increasing trends in human foods and the environment. Environmental contamination by heavy metals has become a worldwide problem during recent years due to the fact that heavy metals unlike some other pollutants are not biodegradable (Bazrafshan *et al*, 2015). Consequently, they are not detoxified but are bio accumulated in the environment. Heavy metals are released into the environment through man's industrial, domestic and commercial activities, industrial effluents, pesticides and fungicides as well as manure from poultry farms (Ukpong, *et al*, 2013). Soil pollution by heavy metals has serious health implication especially with regards to crops/vegetables grown on such soils (Steffana, *et al* 2017). Heavy metals occupy a special position in soil chemistry because they play very important physiological roles in nature (Akpoveta,*et al*, 2010). Generally, topsoil layer contain the largest amount of pollutants. The contaminant concentration in soil mainly depends on the adsorption properties of soil matter. The solubility of heavy metal ions in soil is mainly influence by many factors such as pH, conductivity, moisture content. (Rakesh, and Raju, 2013). As a result of increasing anthropogenic activities, heavy metals pollution of soil, water, and atmosphere represents a growing environmental problem affecting food quality and human health. Heavy metals may enter the food chain as a result of their uptake by edible plants (Shaapera, *et al* 2013). This research work is therefore aim at the determination of heavy metals, Cr, Co, Ni, Pb, Zn, Mn, Cu. in soil around three different tin mining areas of Kapang, selebirom and Sabon angwa all of dorowa district of Barkin Ladi Local govt Area of Plateau State.

MATERIALS AND METHODS

The materials that were used for the research work are: EDX3600B-Energy Dispersive X-ray Fluorescence spectrometer, Jiangsu Skyray information Technology Co. Ltd. China. Oven Galle ham England. Hanna pH 209 and Conductivity meter, Beakers, Mortar and Pestle.

The sampling was done in Dorowa, a village in BarkinLadi Local Government area of plateau state located on Latitude 9.5333 and Longitude 8.9000 where localize tin mining activity is presently ongoing, soil from Kapang, Selebirom and Sabon angwa were collected. At each sampling point, about 0.5kg of the Soil sample was collected from between 0- 20cm from the surface of the soil, using soil auger at a distance of 1m away from each other, and within an area of one square meter. The composite samples collected from the sampling area, were put into polythene bags and then transported to the Laboratory for further treatment.

The pH measurement of the sample was determined with Hanna pH meter 209 using the method describes by Kumar *et al*. (2008). Where 20g of the dried sampled was weighed and transferred into a 20cm³ of distilled water in a 50cm³ beaker.

The mixture was stirred with a glass rod and allowed to stand for 30mins. A pre calibrated HANNA pH meter electrode was then inserted into the solution and the pH was then recorded.

The electrical conductivity (EC) was measured using the modified method of Kumar *et al*. (2008) were 25.00g of the dried sample was placed in a 250cm³ beaker. Distilled water was added slowly drop by drop on the soil sample until it appeared wet. A stirrer was used to homogeneous the soil paste. 50cm³ of distilled water was added to the beaker, covered with a

petri-dish and the mixture shaken for 1hr. 40cm³ of the extract was transferred into 100cm³ beaker. The electrode of the conductivity meter was inserted into the solution to measure the electrical conductivity in µS/cm

The use of ED-XRF was employed in the analysis of the solid samples ED-XRF spectrometry is an elemental analysis technique with broad application in science and industry. XRF is based on the principle that individual atoms, when excited by an external energy source, emit x-ray photons of characteristics energy or wave length. By counting the number of photons of each energy emitted from a sample, the elements present may be identified and quantitated.

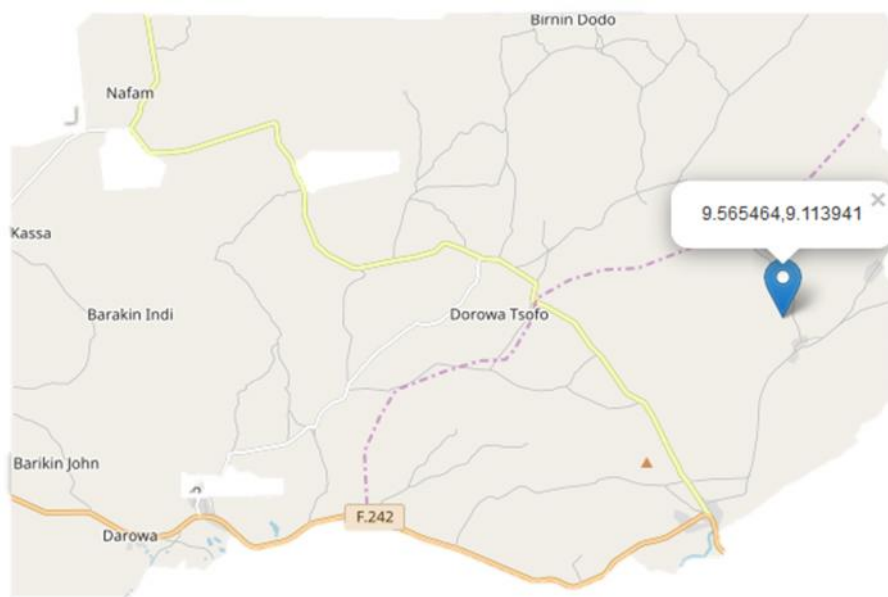


Fig 1: Map of Barkin Ladi Showing Location of the Sampling Area

RESULT

Table 1: pH and Electrical Conductivity value obtained for soil sampled in mining ponds of Dorowa district of Barkin Ladi LGA

Area	pH	Conductivity (µS/cm)
K	2.57	1342
S	6.24	12.42
SA	5.10	20.90
Control	6.60	2.80

Table 2: The result of some heavy metals concentration in Soil around Dorowa District of Barkin Ladi Local Govt. using XRF- spectrometer (mg/kg)

Metal	K	S	SA	C	Max. safe limit in soil (FAO/WHO,2001)
Cr	50.00±0.20	40.01±0.11	16.2±0.43	0.05±0.01	60
Co	902.70±0.14	125.20±0.21	397.60±0.17	0.03±0.00	50
Ni	79.20±0.31	70.01±0.12	76.10±0.11	ND	40
Pb	27.10±0.14	10.10±0.02	67.10±0.23	0.12±0.01	100
Zn	1693.10±0.18	1244.50±0.45	2080.00±0.67	2.50±0.12	100
Mn	145.40±0.11	78.4±0.22	53.10±0.01	18.32±0.17	2000
Cu	65.70±0.08	54.30±0.23	61.40±0.06	2.55±0.05	100

n=3

Key: K= Kapang, S= Selebirom, SA= Sabon angwa C= control

pH

pH is an important factor that influences the bioavailability and transport of heavy metals in soil. The mobility of heavy metals decreases as soil pH increases because hydroxides and carbonates are precipitated or insoluble organic complexes are formed (Archer, 1987). Electrical conductivity is a factor that gives an indication on the amount of dissolve mineral in the soil.

Table 1, Summarizes the pH of Soil in k, S, SA and C as 2.57, 6.24, 5.10 and 6.60 respectively. All the pH are weakly acidic, except for k which is more acidic. This is a strong indication that the heavy metals in the soil of k may be bioavailable.

Cobalt

The result in table 2, reveals that the concentrations of Co, range from 902.70±0.14mg/kg, to 125.20±0.21mg/kg. The maximum value was recorded in k, with the lowest in S, respectively. The levels of Cobalt in this study in all the sampling sites were higher than Ewers, (1991), and Akpoveta *et al*, (2010). The recommended limit of Co in soil is 50mg/kg. Anthropogenic or wide application of pesticides and fertilizer may contribute to the increase in availability of Co in the soil, Ewers, (1991). Nickel is a poisonous heavy metal. The concentration of Nickel in the soil range from 79.20±0.31 mg/kg to 70.01±0.12 mg/kg table 2, these values are higher compared to those reported by Daniel, *et al* (2014) and Akpoveta, *et al*, (2010). According to Rana (2006), in Alshaebi *et al* (2009), Ni contaminates the soil when the concentration of Ni is higher than 40mg/kg. This result shows that the soil is contaminated by Ni. According to Yaron (1996) in Alshaebi *et al* (2009), it is mentions that the highest concentration of Ni is usually found at the top layer of the soil that is rich in organic matter or with relatively high content of clay. Wide application of various types of pesticides and fertilizer may be contributor to the increased in availability of Ni in the soil. Chromium regulates carbohydrate, nucleic acid and lipoprotein metabolism, this metal also potentiates insulin action Yap *et al*, (2010). In addition, Cr activates several enzymes. However, chronic exposure of Cr may damage the liver, kidney and lungs, Malaysian Food Regulation (1985). The range of Cr in the soil is 33.90±0.15mg/kg to 3.30±0.62mg/kg in table 2 which is lower than that of Daniel *et al* (2014). The concentration of Lead (Pb) in the soil sampled in K, S and SA is 27.10±0.14mg/kg, 10.10±0.02mg/kg and 67.10±0.30mg/kg respectively. The highest

concentration is recorded in SA. These values are higher than the one reported by Siti, *et al* (2014) Akpoveta, *et al*, (2010) but lower than Alshaebi *et al* (2009). According to Niragu (1978) in Alsheabi *et al* (2009), the soil is uncontaminated when the concentration of Pb is less than 20 mg/kg. They values obtained from the studies are lower than the FAO/WHO maximum permissible level of 100mg/kg in soil. Pb resides in large quantities with the remnants of mining activities, and the result is an extension of what other studies reported on the Subject, Alshaebi *et al* (2009). The relatively high levels of lead may also have resulted from accumulation of lead through air pollution such as automobile exhaust fumes and from some pesticides, such as lead arsenates applied during cultivation. Zinc and Mn are additionally one of the micro nutrients basic for normal plant development, however just a little amount of these components is required particularly Zn (25-150 µg/g). Zn is the slightest lethal and a basic component in human eating regimen as it is required to keep up the working of the immune defense Latif *et al*,(2018).

Zinc concentration in table 2 ranges from 2080.00±0.67mg/kg to 1244.50±0.45mg/kg this result are higher compared to Latif, *et al*, (2018). It is likely that high concentrations of Zn could be due to oxidation of organic matter and sulfides in the soil in the presence of abundant oxygen (Alshaebi *et al*, 2009). Copper (Cu) has concentration that ranges from 65.70±0.08mg/kg to 54.30±0.23mg/kg in soil, table 2. According to Alloway (1995) in Alshaebi *et al*, (2009), found that if soil has Cu concentration greater than 20 mg/kg, it is considered contaminated soil. This shows that the results of analysis of soil from the study area are found to be contaminated by Cu. Heavy metals contained in the mines tailings are mobilized and migrate to the surroundings and cause severe and widespread contamination of soils, surface and ground waters. Manganese (Mn) is frequently an abundant constituent of soils, but its low solubility at neutral and alkaline pH prevents excessive uptake by plants. Therefore, manganese toxicity is nearly always associated with acid soils Manganese concentration in table 2 has a range of values from 145.40±0.11 to 53.10±0.01mg/kg. The high manganese values in the study area indicated the high availability of Mn for plant uptake area.

One-way analysis of variance (ANOVA) was made at 95% confidence level. The results showed that there was significant differences ($p < 0.05$) in the concentrations of the heavy metals Zn, Cu, Mn, Co, Cr and Ni among the analyzed soil samples while there was no significant difference ($p > 0.05$) in the concentrations of Pb

Table 3. Correlation coefficient (r) for heavy metals concentration in soil sampled

	Zn	Mn	Cu	Co	Ni	Cr	Pb
Zn	1						
Mn	0.576	1					
Cu	0.650	0.595	1				
Co	0.385	0.813	0.952	1			
Ni	0.683	0.559	0.999	0.937	1		
Cr	-0.654	0.884	0.151	0.447	0.106	1	
Pb	0.963	-0.290	0.221	0.069	0.462	-0.833	1

Significant "r" at $p < 0.05$ level

Correlation Analysis

Pearson's correlation coefficient was used to examine the relationship between the various heavy metals in the soil samples from all the sample sites. Table 3 shows the correlation matrix of the relationship between heavy metals concentration of soil samples. Rakesh and Raju (2013) reported that high correlation coefficient (near +1 or -1) means a good relation between two variables, and its concentration around zero means no relationship between them at a significant level of 0.05%, it can be strongly correlated, if $r > 0.7$, whereas r values between 0.5 and 0.7 shows moderate correlation between two different parameters.

As can be seen from Table 3, the results of the correlation coefficients showed strong positive correlation between Co with Mn ($r = 0.813$), Co with Cu ($r = 0.952$), Ni with Cu ($r = 0.999$), Ni with Co ($r = 0.937$), Cr with Mn ($r = 0.884$) and Pb with Zn ($r = 0.963$). This strong positive correlation shows that the elements are closely associated, thus suggesting their common origin. There were also moderate positive correlations Mn with Zn ($r = 0.576$), Cu with Zn ($r = 0.650$), Cu with Mn ($r = 0.595$), Ni with Zn ($r = 0.683$), and Ni with Mn ($r = 0.559$). Strong negative correlations were found between Pb with Cr ($r = -0.833$). Moderate negative correlations were found between Cr with Zn ($r = -0.654$). The other elements have weak negative or positive correlation indicating that the presence or absence of one element affect in lesser extent to the other.

CONCLUSION

The concentrations of heavy metals in soil sample in the study area indicates that the soils serve as the potential source of the heavy metals in the environment and the concentration of the heavy metals: Co, Zn, and Ni are all above the recommended limit while Cr, Cu, Pb and Mn were lower than maximum tolerable levels. The significance difference and increase in the elemental concentrations may be due to application of various types of pesticides and fertilizer in the vegetable farming areas and the mining activities that was going on when research was conducted. In general, the results also show that the level of contamination of the soils by some of the heavy metals is quite high at present and may not be good for the cultivation of crops and vegetables.

REFERENCE

- Akpoveta, O. V., Osakwe, S. A., Okoh, B. E., Otuya, B. O. (2010) Physico-chemical Characteristics and Levels of Some Heavy Metals in Soils Around Metal Scrap Dumps in Some Parts of Delta State, Nigeria. *Journal of Applied Science and Environmental Management*, 14 (4), 576-660.
- Alshaebi F. Y., Wan Z.W. Y., Samsudin A. R & Alsabahi E. I. (2009). Risk Abandoned Tin Mine in Sungai Lembing, Pahang, Malaysia *EJGE*
- Archer, F and Hodgson, I (1987). *Journal of Soil Science* 38 (3), 421-431
- Bazrafshan, E., Mohammadi, L., Ansari-Moghaddam, A., Mahvi, A.H.-(2015). Heavy Metals Removal from Aqueous Environments by Electrocoagulation Process- A Systematic Review. *Journal Environmental Health Science Engineering* 13, 74, 1-16.
Doi:10.1186/s40201-015-0233-8

- Daniel, V. N., Cundusu, E.S., Chup, J. A and Pius, N. D. (2014). Variation of heavy metals in Agricultural Soil Irrigated with Tin mining water in Heipang District of Barkin Ladi, plateau State Nigeria. *International Journal of Science and Technology* 3 (5) 225-263
- Ewers, U. (1991) Standard Guidelines and Legislative Regulations Concerning Metals and their Compounds. In metals and their compounds in the Environment: Occurrence: Merian, E., Ed. Pp 458-468
- FAO/WHO (Codex Alimentarius Commission), (2001). *Food Additives and Contaminants. Joint FAO/WHO Food Standards Program, ALINORM 01/12A*, pp 1-289.
- Haliru, H. A., Ling, L. P., Suhaiza, S. O. (2014). Heavy Metal Concentration Levels in Soil at Lake Geriyo Irrigation Site, Yola, Adamawa State, North Eastern Nigeria. *International Journal of Environmental Monitoring and Analysis* 2, 106-111.
- Heidarieh, M., Maragheh, M.G., Shamami M. A. Behgar, M., Ziaei, F., et al. (2013) Evaluate of heavy metal concentration in shrimp (*Penaeus semisulcatus*) and crab (*Portunus pelagicus*) with INAA method. *Springerplus* 2: 72.
- Kachenko, A.G and Singh, B. (2006) Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia. *Water Air Soil Pollution* 169: 101-123.
- Keesstra, S. D.; Geissen, V., Mosse, K., Piirainen, S., Scudiero, E., Leistra, M., Schaik, L.V. (2014). Soil as a Filter for Groundwater Quality. *Current Opinion on Environmental Sustainability* 4 (5), 507-516.
- Keesstra, S. D., Bouma, J., Wallinga, J., Tittonell, P., Smith, P., Cerda, A.; Montanarella, L.; Quinton, J. N., Pachepsky, Y., Putten, W. H. V., Bardgett, R. D.; Moolenaar, S., Mol, G., Jansen, B., Fresco, L.O.(2016). The Significance of Soils and Soil Science towards Realization of the United Nations Sustainable Development Goals. *Soil*. 2, 111-128.
- Kumar, G. P., Yadav, S. K., Thawale, P. R., Singh, S. K. and Juwarkar, A. A. (2008). Growth of *Jatropha curcas* on heavy metal contaminated soil amended with industrial waste and *Azotobacter* – A greenhouse study. *Bioresource Technology*, 99(6): 2078-2082
- Malaysian food regulation, (1985). Kuala Lumpur; MDC publisher's printers, Sdn bhd, 1996
- Latif A., Bilal M., Asghar W., Azeem M., Ahmad M.I, et al. (2018) Heavy Metal Accumulation in Vegetables and Assessment of their Potential Health Risk. *Journal of Environmental Analytical Chemistry* 5: 234.
- Oresegun, M. D. and Babalola, I. A (1993). The environmental gamma radiation of Jos, Nigeria. *Nigeria Journal of Science* 27: 263-268
- Rakesh, S. M.; Raju, N.S. (2013). Correlation of Heavy Metal Contamination with Soil Properties of Industrial Areas of Mysore, Karnataka, India by Cluster Analysis. *International. Res. Journal Environment Science*, 2 (10), 22-27.
- Siti, N. M. R., Sharizal, H., Mohd, L. K., Norshahrizan, M. H. (2014). Analysis and Pollution Assessment of Heavy Metal in Soil Perlis. *Malaysian Journal of Analytical Science*. 18 (1) 155-161
- Steffana, J. J., Brevika, E. C., Burgess, L. C., Cerda, A. (2017). The Effect of Soil on Human Health: an Overview. *Eur. Journal of Soil Science*, 1-13.

Shaapera, U., Nnamonu, L. A., Eneji, I. S. (2013). Assessment of Heavy Metals in *Rana esculenta* Organs from River Guma, Benue State Nigeria. *American Journal Analytical Chemistry*, 4 (09), 496–500.

Yap, C. K., Fitri, M. M., Mazyhar, Y. and Tan, S. G. (2010). *Sains malaysia* 39 (3) pp 347-352.