Assessment of Heavy Metal Distribution and Concentration in Mining Sites (Du and Zawan) in Jos, Nigeria.

Agboola, C. K; Abata, E. O; Ogunyemi, O. J, Adebayo, A. O

Department of Chemistry, Federal University of Technology, Akure

Abstract

The purpose of this study was to assess the concentration of heavy metals in abandoned mined sites around Du and Zawan in Jos South local government. A total of 30 soil samples were collected from the site at depth 0 to 15cm and two (2) common plant produce were collected for this study. The samples were subjected to standard methods and the heavy metals were analysed using Atomic absorption spectrophotometer. The statistical analyses were conducted using one way analysis of variance. The pH of the Du and Zuwan site is $5.33^a \pm 0.09$ and $5.43^a \pm 0.02$. The CEC of the soil samples in Du and Zawan is $6.31^a \pm 0.11$ and $6.47^a \pm 0.10$ respectively.

Keywords: Heavy metals, contamination, pH, concentration, and mining sites

Introduction

Mining has long been ascribed as one of the major contribution of heavy metals to the environment. Due to its advancements in technology, it has led to the rapid increase of toxic heavy metals into the environment and this can be evidence in the amount of soil erosion and devastation of the environment during and after mining. Mining activities has to do with extraction, beneficiation and processing of minerals. Mining activities are responsible for an increase in certain heavy metals in soils, sediments and groundwater reserves occurring within the influence sphere of the mine (Daniel, 2014). The activities give rise to non-biodegradable nature of heavy metals which persist for a long time in soil and interfere with normal metabolic activities of living organism. Therefore, this heavy metal enters the body system through food, water and air and tends to bio-accumulate.

When heavy metal gets to the soil, it undergoes different reactions with other soil components which tend to affect their availability, mobility, solubility and transportation in the environment (Scokart *et al.,* 1983). Many of the heavy metals are essential at low concentrations for plant and animal including human health but at higher concentrations, they can be very toxic.

The continuous accumulation of heavy metals in soils surrounded by mines will result in increased heavy metal uptake by plants. This is disturbing because of potential health risk to the people living in that environment (Pruvot *et al*., 2006). The presences of these metals in the environment have resulted to damages to tissues and organs such as the central nervous system, the cardiovascular and gastrointestinal (GI) systems, kidneys, liver, and bones, the risk of cancer.

In Jos South, Plateau state Nigeria, the mining of tin started in 1902 and has been responsible for the drastic changes in the landscape and economic structure of the vicinity (Michael, 2012). The main occupation of people living in this vicinity is farming and the food grown in the area include root tubers, cereals and vegetables which are often times irrigated from streams and dams from the mining sites. Most crops grown on the mined soil are mostly low agriculturally, quick in maturing and have low nutrients leading to yellowish leave, stunted growth etc. It is necessary to understand how the release of toxic heavy metals from the mined soil enters the food chain since the toxicity cannot be neglected. In view of the serious health hazards posed to man, especially through the inhalation and ingested pathway, their concentration if not carefully regulated, may lead to accumulation in man (Abidemi and Theresa, 2015). Hence, there is need to assess the heavy metal distribution and concentration of heavy metals in old mining sites (Du and Zawan) in Jos South Local Government area.

MATERIALS AND METHODS

The studied areas are located in Jos South local government area of plateau state (Du and Zawan). The communities lies between latitudes $8^0 50'$N and $9^0 00$N and longitudes $9^0 45'$E and $9^0 50'$E. (Figure 1). The study area as shown is a rural community of population of 306,716. It's well known for their agricultural contribution to the state. The Du sample $9^0 50' 23.2''$N $8^0 54' 48.6''$E; Zawan: $9^0 50' 4.6''$N $8^0 52' 29.5''$E and Control $9^0 50' 38.1''$N $8^0 53' 48.3''$ E.
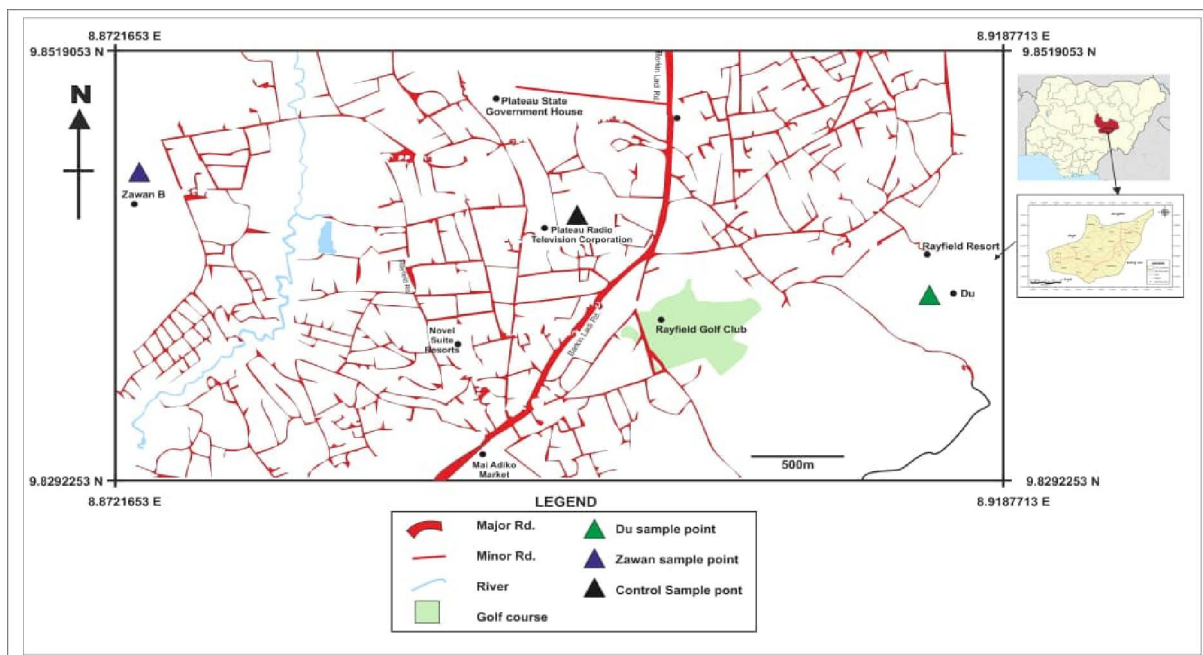
Description of site

Figure 1: Map showing the site description

Samples Collection and Preparation

A total of thirty (30) soil samples were collected in a random system from each site at a depth of 0-15 cm and using a stainless steel soil auger. The samples were transferred into polyethylene bags and labeled for easy identification. Also, the plant produce (maize and beans) common to the sites were collected in black polyethene bags, tied and labeled. The soil and plant produce were taken to the laboratory. The soil samples were air-dried for seven days after which they were ground into powdered form with the aid of mortar and pestle. The samples were sieved through a 2.0 mm sieve to obtain a homogenous particle of the same surface area, which was later kept in plastic containers and covered prior to analysis. The plant produce was subsequently dried, ground to fine powder with the aid of mortar and pestle and stored prior to analysis.

METHOD

Soil Analysis

The soil pH and electrode potential was determined by Gungshik *et al.,* 2007. The particle size analysis was measures using a hydrometer. The conductivity was measured using a conductivity meter). The Cation Exchange Capacity (CEC) was determined using the method of Inengite *et al.,* 2015, while the Organic matter content was determined sing the Walkley – Black method.

Total metal analysis of soil

One gram of each soil samples was weighed in a 100 ml clean Kjedahl digestion flask, 20ml of the mixture of concentrated nitric acid HNO_3 and concentrated hydrochloric acid HCl in a ratio of 1:3 was added and

was then heated in a fume cupboard until a slightly clear color solution was obtained. It was cooled and filtered using Whatman filter paper into a 50ml standard flask and made up to mark with deionized water. The digests were analyzed using Atomic Absorption Spectrophotometer (AAS) in appropriate instrumental conditions.

Sequential extraction analysis
Modified version of Tessier *et a*l., (1979) was adopted for the chemical fractions of the soil for the determination of sequential extraction:

F1.   Exchangeable fraction:
The soil sample was extracted for 1 hr with 16ml of 1M magnesium chloride solution at pH 7.0 with continuous agitation. The solution was allowed to settle and then filter.

F2.   Metal bound to carbonate
The residual from exchangeable fraction extraction was leached at room temperature with 16ml of 1M sodium acetate solution adjusted to pH 5.0 with acetic acid. Continuous agitation was maintained for 5 hrs. The solution was also allowed to settle and then filtered.

F3.   Metal bond to Fe-Mn oxide
The residue from metal bound to carbonate fraction was extracted with 20ml of 0.04 M $NH_3OH.HCl$ in 20ml of 25% (v/v) acetic acid and was heated to 96^0C with occasional agitation for 6 hrs.

F4.   Metals bound to Organic Matter
The residue from metal bound to Fe-Mn oxide was extracted with 3ml of 0.02M HNO_3 and 5ml of 30% H_2O_2 adjusted to pH 2.0 with nitric acid and the mixture was heated to 85^0C for 3 hrs with intermittent agitation. The mixture was cooled and 5ml of 3.2M ammonium acetate in 20% (v/v) nitric acid (HNO_3) was added and the sample was diluted to 20ml and agitated continuously for 30 mins.

F5.   Residual fraction
The residue from metal bound to organic was digested in a Teflon beaker with a mixture of 5 ml concentrated nitric acid, 10 ml of hydrofluoric acid and 3 ml of perchloric acid. The extracts from each step was filtered into a 50ml standard flask and were analyzed using Atomic Absorption Spectrophotometer (AAS) in appropriate instrumental conditions. Triplicate determinations were made for each fraction in addition with a blank sample.

Total metal analysis of maize and bean obtained from the tailing site
One gram of each plant samples was weighed in a 100 ml clean Kjedahl digestion flask, 20ml of the mixture of concentrated nitric acid HNO_3 and concentrated hydrochloric acid HCl in a ratio of 1:3 was added and was then heated in a fume cupboard until a slightly clear color solution was obtained. It was cooled and filtered using Whatman filter paper into a 50ml standard flask and made up to mark with deionized water. The digests were analyzed using Atomic Absorption Spectrophotometer (AAS) in appropriate instrumental conditions.

RESULT AND DISCUSSION

Table 1: Physico-chemical analysis of soil.

Sample	pH	EC	Eh	CEC	OM	Silt (%)	Clay (%)	Sand (%)
1	$5.33^a\pm0.09$	$33.7^a\pm1.16$	$82.7^b\pm1.52$	$6.31^a\pm0.11$	$3.81^b\pm0.14$	$32.2^b\pm6.39$	$10.6^a\pm2.53$	$59.9^a\pm1.12$
2	$5.43^a\pm0.02$	$36.7^a\pm2.31$	$81.7^b\pm1.53$	$6.47^a\pm0.10$	$2.22^a\pm0.17$	$30.5^b\pm0.04$	$11.4^a\pm1.18$	$57.9^a\pm1.14$
3	$6.14^b\pm0.39$	$94.3^b\pm1.15$	$49.7^a\pm1.53$	$6.66^b\pm0.03$	$2.04^a\pm0.10$	$17.4^a\pm1.44$	$17.9^b\pm1.28$	$64.7^b\pm2.73$

Sample 1= Du, Sample =2: Zawan and Sample 3= control; Eh= Electrode potential; EC= Electrical conductivity; CEC= Cation Exchange Capacity; OM= Organic matter; pH

The physiochemical analysis of the soil

The pH values of the soil samples are represented in Table 1. Although, the pH of the soil samples are slightly acidic. The table show that both soil samples have a slightly higher pH than the control. For most plants, the soil pH below 6.0 is undesirable and need to be raised with liming materials to raise their pH to near neutral level. The pH of the Du and Zawan site is $5.33^a\pm0.09$ and $5.43^a\pm0.02$. The Electrode potential measures the degree of reduction in the soil and the number of free electrons exchanged in the redox

reaction. From the above table, the electrode potential of the Du and Zuwan is lower than the control. CEC represents the ability of the soils to withhold or release cations and it is an important parameter in this study. The CEC of the soil samples in Du and Zawan is 6.31[a]±0.11and6.47[a]±0.10 respectively. The soil organic matter improves soils usefulness for agricultural purposes. From the above table, the organic matter present in the soil is relatively low. Organic matter supplies major nutrients and acts as a source of food to microbes and thereby helps to improve and control their activities (Brady and Weil, 1996).

Table 2:　Sequential extraction of the heavy metals in tailing samples.

Metal	Location	F1	F2	F3	F4	F5	∑ F1 – F5	% Recovery
Cu	1	ND	0.02±0.00	3.90±0.203	0.97±0.02	4.65±0.01	12.10	78.80
	2	0.03±0.001	0.33±0.012	1.89±0.10	3.57±0.02	5.28±0.01	11.11	75.11
	3	ND	ND	3.54±0.18	1.41±0.40	4.1±0.40	9.05	95.62
Cr	1	ND	ND	1.46±0.02	1.63±0.02	8.54±0.05	11.63	77.47
	2	ND	ND	ND	ND	5.97±0.29	5.97	0.00
	3	ND	ND	ND	ND	3.96±0.02	4.96	0.00
Cd	1	1.23±0.01	0.83±0.02	ND	ND	ND	2.10	82.35
	2	1.28±0.00	1.53±0.01	ND	ND	ND	2.80	91.80
	3	ND	ND	ND	ND	ND	0.00	0.00
Pb	1	ND	ND	ND	ND	4.68±0.17	4.68	83.26
	2	ND	ND	ND	ND	7.14±0.25	7.14	67.29
	3	ND	ND	ND	ND	2.35±0.59	2.35	58.03
Zn	1	7.29±0.04	6.11±0.00	5.50±0.03	3.00±0.03	13.97±0.03	35.54	98.26
	2	10.48±0.02	10.20±0.03	5.26±0.02	4.23±0.06	11.10±0.27	41.26	97.69
	3	9.09±0.31	5.21±0.04	5.30±0.02	3.38±0.02	7.93±0.04	30.90	93.88

Sequential Extraction of the Soil Tailing
The exchangeable fraction, sometimes referred to as the acid-soluble/water soluble fraction, is
envisaged to comprise water-soluble elements as well as ion (H+) exchangeable and carbonate bound metals. This fraction represents the natural environmental effects of acidic rainwater percolation (Anju *et al*., 2010). These metals

are also considered to be mobile and can be used to quantify the short term availability for leaching or uptake by plants (Brumer *et al.*, 1986). Zinc was observed to be highest in the Du and Zuwan site with exchangeable fractions of 7.29±0.04 and 10.48±0.02respectively. Carbonation by absorption of atmospheric CO_2 and addition during any waste processing steps (such as by the addition of lime) results in significant carbonate abundance in many waste streams. This can lead to redistribution of element associations, and when introduced to soil most of the metals will associate or complex with the carbonates present, despite the presence of other reactive phases. Zn also shows a high complex formed with the carbonate and also a high complex formed with the Fe-Mn oxides which shows that the soil sample has high zinc content other than other element. The reducible (Fe-Mn oxides) fraction represents metals bound to iron and manganese (and sometimes aluminum) oxides that would be released if the solid matrix were susceptible to anoxic (reducing) conditions. The residual fraction is where metals have the strongest associations with crystalline structures of primary and secondary minerals, *i.e.*, they are the most difficult to extract and Zn is shows the highest in comparison with other metal. This fraction is relevant in the assessment of long-term risk of PTEs.

Table 3:   Total Heavy metal concentration (mg/Kg)

Location	Cu	Zn	Cr	Cd	Pb
Site 1	12.10[b]±0.32	36.54[a,b]±0.15	15.02[b]±0.05	2.55[b]±0.01	5.62[a,b]±0.02
Site2	14.79[b]±0.02	42.24[b]±0.17	9.95[a,b]±0.05	3.05[b]±0.02	10.62[c]±0.04
Site3	9.47[a]±0.07	32.92[a]±0.53	6.82[a]±0.13	0.00	4.05[a]±0.02

Values are mean ± SD (n=3)

Total Heavy Metal Concentration (mg/kg) of the Tailing

The Total concentration of metals analyzed for the mining sites and the control site indicates the different properties of soil. The metals analyzed are Copper (Cu), Zinc (Zn), Chromium (Cr), Cadmium (Cd), Lead(Pb). From the above table, Zinc is high in site 1 and site 2 with concentration of 36.54[a,b]±0.1and 42.24[b]±0.17 respectively. The high zinc concentration is also observed in the control site. The low concentration of copper as observed from the result may be due to the mobility of Cu in weathering environment and also due to the ability of Cu to adsorb onto soil constituents surfaces through ion exchange process (Wuana and Okieiman, 2011).

Heavy metal analysis of the maize and beans obtained in the soil tailing

Figure 2 and figure 3 shows the heavy metal concentration on the plants obtained from the Du and Zuwan tailing sites. In both sites, Pb, Cd and Cr are not detected in the plants. Zinc is observed to be high in the maize and beans plants obtained as compared to the control site. The maize and beans plants also shows a significant amount of copper concentration in the plants. The mean concentrations of the sites were greater than that of the control site, indicating some degree of contamination of the study site.
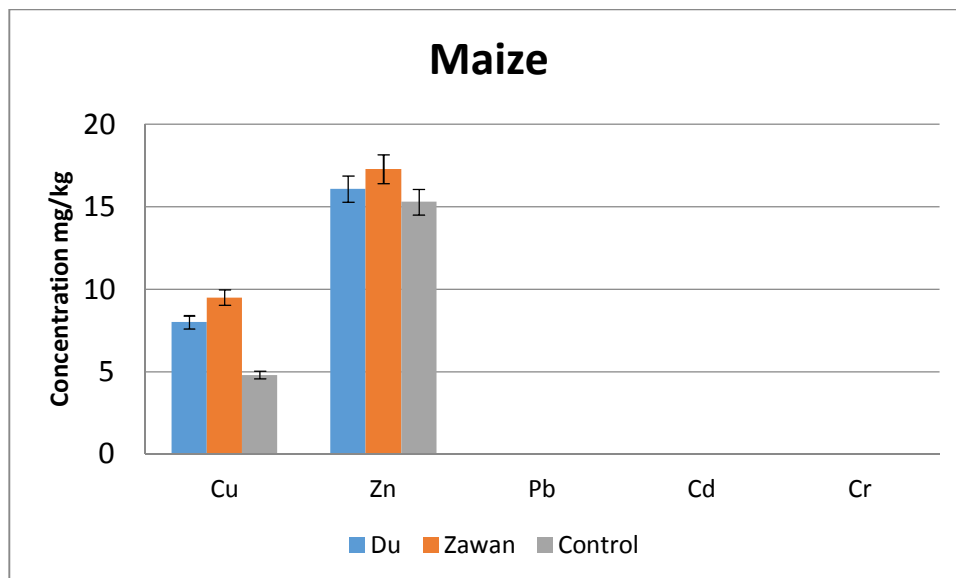
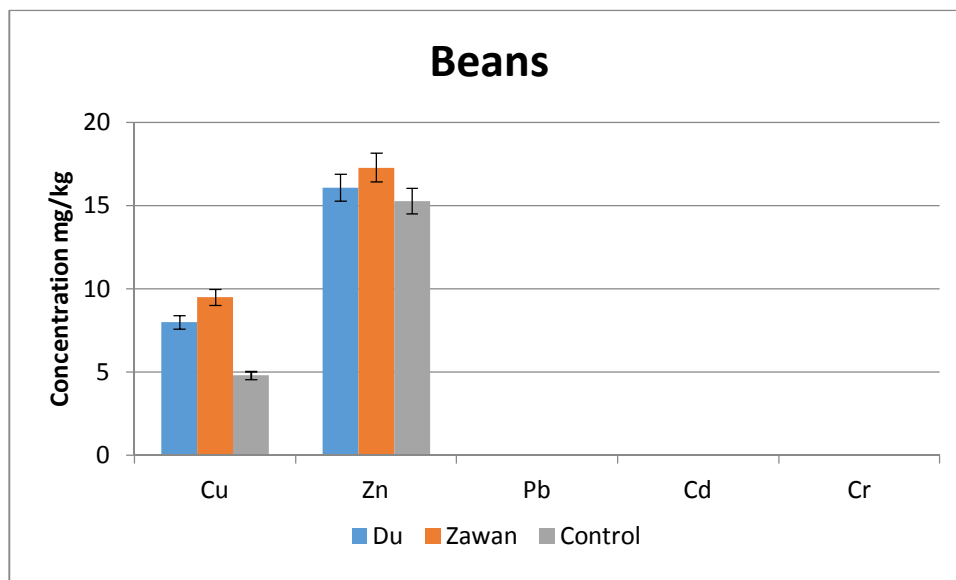**Figure 2: Mean Concentrations (mg/kg) of Heavy metal in Maize Sample**

Figure 3: Mean Concentrations (mg/kg) of Heavy Metal in Beans Sample

CONCLUSION

The results obtained for total metal determination shows that zinc is higher in the mining sites when compared to the control. The soil electrode potential and the pH shows the soil carbon persistence and gives information on the presence of chemical compounds needed by the soil for growth, especially in most organic soil and this was observed to be lower in Du and Zawan when compared to the control site. The results also show that lead, cadmium

and chromium were not present in the plants obtained from the sites.

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REFERENCE

[1]. Abidemi, O. O., and Theresa, O. C. (2015). Environmental Fate of Heavy Metals in Soil of Ido- Osun Waste Dump Site, Osogbo, Osun, Nigeria. *American Journal of Environmental Protection*, *3*(1), 1-4.

[2]. Anju, M.; Banerjee, D.K. Comparison of two sequential extraction procedures for heavy metal partitioning in mine tailings. *Chemosphere* **2010**, *78*, 1393–1402.

[3]. Brumer, G.W.; Gerth, J.; Herms, U. *Heavy Metal Species, Mobility and Availability in Soils*; Bodenk, Z.P., Ed.: Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 1986.

[4]. Daniel, V. N, Chudusu, E. S., Chup, J. A and Pius, N. D. (2014). Variations of heavy metals in agricultural soils irrigated with tin water in Heipang district of Barkin Ladi, Plateau state, Nigeria. International Journal of Science and Technology, 3 (5): 255-262.

[5]. Gungshik, J. R., Lohdip, Y. N., and Bewarang, E. S. (2007). Speciation of Trace Metals in Top Soils in Jos Industrial Areas.

[6]. Inengite, A. K., Abasi, C. Y., and Walter, C. (2015). Application of pollution indices for the assessment of heavy metal pollution in flood impacted soil. *Int. Res. J. Pure Appl. Chem,* 8(3), 175-189.

[7]. Jacob, J. O., Kakulu, S. E., Paiko, Y. B., Adeyemi, H. R.Y., And Ndamitso, M. M. (2015). Determination of bioavailiable concentrations of Cu and Zn in farm soils in Kaduna Metropolis, Nigeria. *Ife Journal of Sci.* Vol 17, No 1.

[8]. Michael Adejare Adegboye (2012). Effect of mining on farming in Jos South Local Government Area of Plateau State. *Journal of Soil Science and Environmental Management* Vol. 3(4), pp. 77-83 DOI: 10.5897/JSSEM11.048

[9]. Scokart, P.O., Meeus-verdinne, K. and De Borger, R. (1983) Mobility of heavy metals in polluted soils near zinc smelters. *Water, Air Soil Pollut.*, 20, 451– 463.

[10]. Tessier, A., Campbell, P. G., and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. Analytical chemistry, 51(7), 844-851.

[11]. Tripathi, A., and Misra, D. R. (2012). A study of physico-chemical properties and heavy metals in contaminated soils of municipal waste dumpsites at Allahabad, India. *International Journal of Environmental Sciences*, *2*(4), 2024.

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