

Spectrophotometric Evaluation of Heavy Metal Speciation in Lead-Zinc Mine Soil from Enyigba in Ebonyi State

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Abstract: Soil contamination by heavy metal poses threat to the environment and renders the land less valuable. The heavy metal speciation in a Pb-Zn mine soil of Enyigba in Ebonyi State has been studied using Varian AA240 Spectrophotometry. A five-step sequential extraction procedure adopted by Tessier, Campbell and Bisson was modified for the extraction of the various fractions of the metal. Results obtained showed that total heavy metals assayed were all higher than the WHO recommended limit in soil except Cu (1.79ppm) which is within the WHO limit of 2.00ppm. The highest concentration of Zn, Pb, Mn, Cu, As, Cd, and Cr were obtained in the residual (F5) fraction, 20.04, 11.68, 20.32, 0.68, 19.54, 0.70 and 0.56 respectively. While Fe has the highest concentration in the exchangeable fraction (66.24).

Key words: Heavy metal, Enyigba Lead-Zinc Mine, Soil

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I. Introduction

It is now generally accepted that the distribution, mobility, toxicity and biological availability of chemical elements wholly depends on their concentrations and states of occurrence (Ure, 1993). This helps to ascertain the physical and chemical associations that they exist in natural systems. Changes in environmental conditions; natural or anthropogenic can strongly influence the behaviour of essential and toxic elements by altering the states in which they occur (Templeton *et al.*, 2000). The total heavy metal contents of the soil indicate the extent of contamination, but the heavy metal concentrations in solution mostly determine the actual environmental exposure or risk. Knowledge of the distribution of heavy metals between the soil and solution is essential for evaluating environmental impact. Quantifying the total concentration and chemical speciation can be used to characterize the behaviour of heavy metals in soils (Iwegbue, 2011).

Chemical and biological processes can mobilize these heavy metals to contaminate water supplies and find their ways into food chains. The major pathway of soil pollution is through atmospheric deposition of trace metal from their point of sources such as metalliferous mining, smelting processes and other industrial activities. Other sources of pollution affect severely agricultural soils/lands and they include inputs such as fertilizers, pesticides, sewage sludge, organic manures and composts manures (Singh, 2001). Uptake of metals by plants is dependent on chemical form of the metals in the polluted soil/land. High levels of trace metals in soils causes their uptake by native and agronomic plants (Li *et al.*, 2000). Plant roots are the important site for uptake of chemicals from soil (Musah, 2008). At different stages, dependent on specie, plants have the ability to extract or remediate toxins from soil through their root systems (Musah, 2008).

Plants grown in Pb, As, Cr, Zn and Cu polluted soils phytomines abundant portion of metals through their roots (Stalikaset *et al.*, 2008). The high level of heavy metal in the soil could indicate similar concentration in plant by accumulation at a concentration that causes serious risk to human health when consumed (Singh *et al.*, 2010). Heavy metals are considered environmental pollutants because they are non-biodegradable and toxic in nature, their degree of toxicity varies from metal to metal and from organism to organism (Duffins, 2002). Heavy metal accumulation in plants, especially consumable tuber crops occurs at high concentration which may exceed recommended safety levels thereby posing health hazards to man and environment (Uriah *et al.*, 2014).

This research is aimed at studying the bioavailability, bioaccumulation and mobility of Zn, Pb, Fe, Mn, Cu, As, Cd, and Cr in Enyigba mining location and the toxicity of these heavy metals. This research will be very instrumental to Government in placing rural area development scheme, enacting environmental protection laws and choice of techniques to be employed in soil remediation. This work would also be very useful to the inhabitants of Enyigba community, who may be curious about the toxic effect of the heavy metals in the environment.

Area of Study

Enyigba is a local village which is 14km from Abakaliki, Ebonyi State which lies in the coordinate of 6.3231° N, 8.1120° E located in the South-East region of Nigeria. The prevalent climate of Enyigba are high precipitation that exceeds evapotranspiration rates, high temperatures and humidity for more than half the year. Vegetation types are mangrove and freshwater swamp communities, rainforest, forest/savanna mosaic and derived savanna zone. Farming systems dominate in the region are yam, plantain crops, potatoes and cassava with oil palm bush and indigenous trees of nutritional, economic, medicinal and cultural importance (Microsoft Encarta, 2007).



Figure 1. Map of Nigeria showing the study area (Abakaliki), adapted from Microsoft Encarta (2007)

Soil Sample Collection and Preparation

Soil samples (n=8) from Enyigba Lead-mine environment were randomly collected at 0-50cm depth at different points within the mining location. The samples were mixed to form a composite sample. Stones, leaves, roots and other materials extraneous to the soil were removed. The composite sample was oven dried at 105°C and ground with pestle and mortar. The ground sample was passed into a sieve of 2mm mesh size, homogenized and stored at 4°C until needed.

Analysis of Soil Samples

1. Fraction 1: Exchangeable

The exchangeable fraction was extracted at room temperature by measuring 2.0g of soil sample into a 16mL of MgCl₂ (pH 7.0) followed by agitation using a centrifuge machine (GULFEX Model HNSII CFC 301) at 4000rpm for about 1 hour (Tessier *et al.*, 1979)

2. Fraction 2: Bound to Carbonate

The residue from (i) was leached at room temperature with 16 mL of 1 M Ammonium acetate (adjusted to pH 5.0 with acetic acid). Continuous agitation was maintained for 5 hours.

3. Fraction 3: Bound to Fe-Mn Oxides (Reduced)

The residue from (ii) was extracted with 40 mL of 0.04 M NH₂OH.HCl in 25% (v/v) Acetic acid at 96°C with occasional agitation for 6 hours.

4. Fraction 4: Bound to Organic Matter (Oxidized)

To the residue from (iii) were added 3 mL of 0.02 M HNO₃ and 5 mL of 30% H₂O₂ (adjusted to pH 2 with HNO₃), extraction was done by heating the mixture to 85°C for 3 hours with occasional agitation. A second 3 mL aliquot of 30% H₂O₂ (pH 2 with H₂SO₄) was then added and the sample was heated again to 65°C for 3 hours with intermittent agitation. After cooling, 5 mL of 3.2 M NH₄OAc in 20% (v/v) HNO₃ was added and the sample was diluted with distilled water to 20 mL and agitated continuously for 30 minutes. The addition of NH₄OAc is designed to prevent adsorption of extracted metals onto the oxidized sediment (Nissenbaum and Kaplan, 1972).

5. Fraction 5: Residual

The residue from (iv) was digested with a 20mL HNO₃-HClO₄ mixture for total metal analysis. Temperature was slowly risen until reflux condition and maintained for 2 hours on a hot plate. After cooling, 2% HNO₃ was used to make up to 50mL.

After each successive extraction, separation was done by centrifuging (GULFEX Model HNSII CFC 301) at 4000rpm. The supernatants were filtered and analysed for heavy metals. The residue was washed with 16mL of distilled water and followed by centrifugation before the next extraction. All glassware used for the experiments was previously soaked in 14% HNO₃, (v/v) and rinsed with deionized water. All reagents used in this study were of analytical grade.

Trace Metal Analysis. Trace metal concentrations were determined by atomic absorption spectrophotometry (Varian AA240). involving direct aspiration of the aqueous solution into an air-acetylene flame. For the metals present in high concentrations (Fe and Mn) the supernatant solution was diluted ten times with deionized water and the concentrations were obtained directly from appropriate calibration curves prepared with the components of the extraction solution diluted by the same factor. The filtrates were made up to 100mls mark in volumetric flasks with distilled water.

II. Results

Table 1: Replicate determination and mean for total metal content in soil sample

Metals	Mean±StDev*	WHO(ppm)
Zn	36.45±0.095	3.00-5.00
Pb	86.34±1.160	0.01
Fe	193.40±1.313	0.30
Mn	128.17±0.969	0.05
Cu	1.79±0.0001	2.00
As	35.27±0.084	0.05
Cd	1.85±0.0001	0.10
Cr	1.73±0.0001	0.05

TMC = Total Metal Concentration

Table 2: Mean value of the speciation of heavy metals on impacted soil

Metals(ppm)	Exchangeable Fraction (F ₁)	Carbonates (F ₂)	Reduced Fraction (F ₃)	Oxidized Fraction (F ₄)	Residual Fraction (F ₅)	Sum of the Fractions	
Zn	6.04	2.47	2.60	2.58	20.04	33.73	
Pb	5.62	1.23	1.14	2.05	11.68	21.72	
Fe	66.24	7.60	65.00	31.24	17.50	187.58	
Mn	18.61	1.22	41.40	38.52	20.32	120.07	
Cu	0.24	0.02	0.32	0.22	0.68	1.48	
As	5.88	2.22	2.50	2.62	19.54	32.76	
Cd	0.10	0.32	0.45	0.24	0.70	1.81	
Cr	0.21	0.05	0.50	0.32	0.56	1.64	pH= 6.70

Table 3: Mean value of the speciation of heavy metals on control soil

Metals (ppm)	Exchangeable Fraction (F ₁)	Carbonates (F ₂)	Reduced Fraction (F ₃)	Oxidized Fraction (F ₄)	Residual Fraction (F ₅)
Zn	1.21	1.40	1.51	1.65	12.03
Pb	2.15	0.16	1.02	1.28	4.55
Fe	2.12	2.42	3.54	3.65	6.35
Mn	1.60	0.88	2.42	2.01	8.05
Cu	0.05	0.005	0.01	0.11	0.44
As	1.05	1.80	0.25	1.09	1.24
Cd	0.03	0.05	0.30	0.01	0.65
Cr	0.05	0.01	0.50	0.45	1.51
pH= 8.20					

Table 4: Percentage recovery of metals

Metals	Total metals in	Total metal	% Recovery

	soil (ppm)	speciation (ppm)		
Zn	36.45	33.73	92.54	
Pb	19.34	21.72	112.31	
Fe	193.40	187.58	96.99	
Mn	128.17	120.07	93.68	
Cu	1.79	1.48	82.68	
As	35.27	32.76	92.88	
Cd	1.85	1.81	97.84	
Cr	1.73	1.64	94.80	

Figure 1: Mean concentration profile of metals in the soil sample

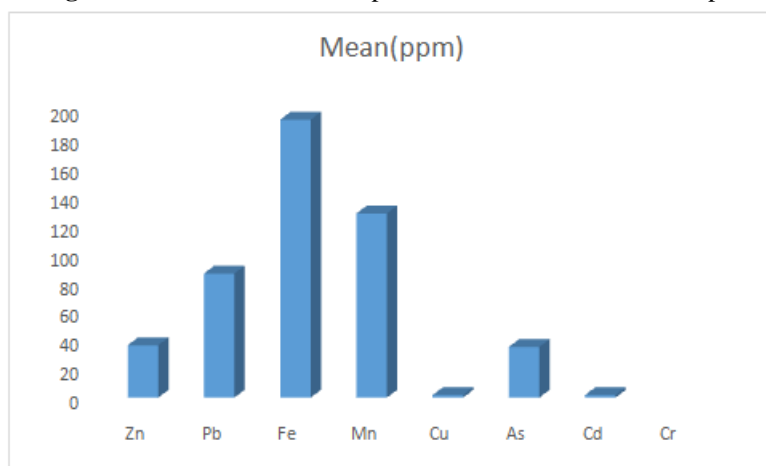
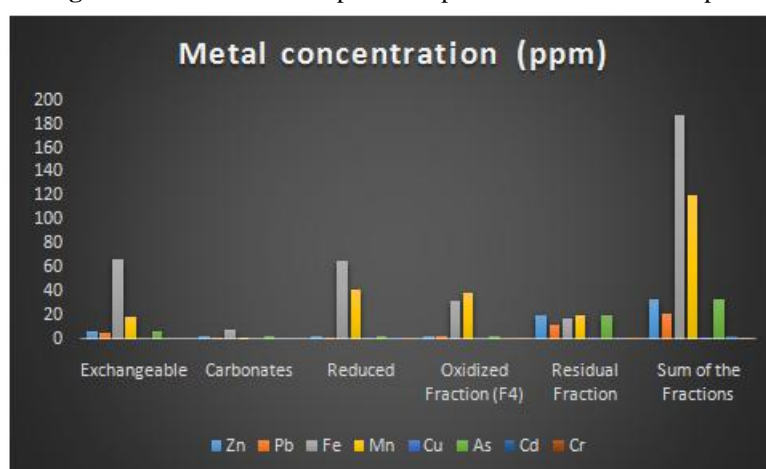


Figure 2: Different metal speciation profile from the soil sample



III. Discussion

The distribution of metal concentration in the soil sample Fe>Mn>Pb>Zn>As>Cd>Cu>Cr is shown in Table 1 and Figure 1. Table 1 also contain the WHO permissible limits of these heavy metals. Zn, Pb, Fe, Mn and As are highly above the WHO permissible limits of 3-5ppm, 0.01ppm, 0.3ppm, 0.05ppm and 0.05ppm respectively. Cd and Cr (1.85ppm and 1.73ppm) are slightly above the WHO permissible limit on soil. Cu among other analysed metals is the only heavy metal within the WHO permissible limit. The heavy metal concentration exceeding the WHO permissible limit suggests possible soil contamination (Wong *et al.*, 2003). The distinct high level of Fe, Mn, Pb and Zn is due to the natural and anthropogenic occurrence of these metals (Ajiwe *et al.*, 2018). High concentration of Fe, Mn, Pb, Zn and As is due to the deposits of Pb-Zn minerals and mining activities in the area (Ogbonna *et al.*, 2015).

The speciation pattern of the metal concentration from the control site (Table 3) as compared to the speciation pattern of the metal concentration from the impacted site (Table 2, Figure 2), showed that the

significant amount of metal concentration from the impacted site on F1, F2 and F3 fractions is as a result of anthropogenic activities in the site, as endogenous and exogenous metals resulting from chemical processes, physical effects and environmental contamination are loosely bound to the soil matrix of the impacted site and can easily be released during speciation (Iwegbue *et al.*, 2006; Abollino *et al.*, 2002).

Zinc

The amount of Zn associated with the fractions from the impacted site ranged from 2.47 – 20.04ppm (Table 2, Figure 2) as compared to the amount of zinc associated with the fractions from the control site, 1.21 – 12.03ppm (Table 3). The order of the concentration of Zn in each of the fractions from the impacted site is $F5 > F1 > F3 > F4 > F2$. The high availability of Zn in the residual fraction (F5) is because Zn have high tendency to become unavailable once it is in soil, hence the residual fraction will have higher amount of Zn concentration (Iwegbue, 2011). Also, the high availability of Zn in the residual fraction (F5) is in agreement with the findings of Brandley and Cox, (1987) which they reported that residual fraction has high retention power of Zn. The lower concentration of Zn in Fe-Mn oxide bound fraction (F3) is due to the Fe-Mn oxide to undergo precipitation and co-precipitation with Zn, this greatly affects the accumulation of Zn in the profile (Zauyah *et al.*, 2004; Broughriet *et al.*, 2007). Soil adsorption of Zn contributes to its mobility and heavy soil contamination and it is always limited to the region of their source (Li *et al.*, 2000). The low availability of Zn in carbonate bound fraction (F2) is in agreement with the findings of Silveira *et al.*, (2006) which he reported that Zn are preferentially bounded to Fe-Mn oxides rather than carbonate bound fraction, this could be as a result of the mineralogy of the soil which could be dominated by sesquioxides (an oxide in which oxygen is present in the ratio of three atoms to two of another element).

Lead

Lead was found to associate more in the residual fraction (F5), 11.68ppm and least distribution was found in the carbonate bound fraction (F3), 1.14ppm. The order of its distribution among the fractions is $F5 > F1 > F4 > F2 > F3$. The amount of Pb from the impacted site is higher compared to the control site, this is as a result of the natural occurrence of Pb in the impacted site and other anthropogenic activities. Pb is the major cause of pollution and contamination in the study area. It is very toxic to the environment, both on plants and animals (Oti *et al.*, 2013). The predominance of Pb in exchangeable fraction, reducible fraction and organic bound fractions is due to the ability of Pb to form stable complexes in each of the phases and this finding is in agreement with the report of Ryan *et al.*, (2002), Iwegbue, (2011) and Kotokyl *et al.*, (2003). Also, Pb has high affinity for soil organic matter (Iwegbue, 2011) which explains the high distribution of Pb through the organic bound fraction.

Iron

The mobilization and distribution of Fe in the impacted site (Table 2, pH = 6.70) among the fractions is in the order, $F1 > F3 > F4 > F5 > F2$ as compared to the control site (Table 3, pH = 8.20), $F5 > F4 > F3 > F2 > F1$. The distribution does not follow a regular pattern as this could be as a result of difference in the pH and soil-water conditions from the impacted site and control site. This is in agreement with the report of Francis *et al.*, (1990), the availability, fixation and mobility of Fe generally depend on the soil pH and soil-water conditions. Soil with high alkalinity promotes the precipitation of Fe^{3+} while soil with high acidity promotes the precipitation of Fe^{2+} (Thompson and Troeh, 1973; Ecological Soil Screening Level for Iron, 2003).

Manganese

The mobilization and distribution of Mn in the impacted site (Table 2) ranged from $F3 > F4 > F5 > F1 > F2$ and $F5 > F3 > F4 > F1 > F2$ (Table 3) in the control site. The Fe-Mn oxide constitute the highest concentration of Mn (41.40ppm), this conforms with the report of Iwegbue, (2011). Mn can readily be adsorbed by plants and utilized in a soil environment. This causes low concentration of Mn in exchangeable and carbonate bound fraction (Teixera *et al.*, 2010). The dominance of Mn in Fe-Mn oxides bound and residual fraction from the impacted site and control site respectively agrees with the findings of Abollino *et al.*, (2002). But the lower concentration of Mn (17.50ppm) in the residual fraction as compared to high Mn (41.40ppm) concentration of the exchangeable fraction from the impacted site disagrees with the report of Iwegbue, (2011).

Copper

Copper is more mobile and well distributed at the impacted site than the control site. The distribution of Cu among the fractions ranged from $F5 > F3 > F1 > F4 > F2$ from the impacted site and $F5 > F4 > F1 > F3 > F2$. The distribution pattern is similar. There is a dominance of Cu in the residual and reduced fraction from the impacted site and residual and oxidized fractions from the control site. Biological activities take place at the superficial horizons and Cu distribution is more within the organic matter bound fractions (Abollino *et al.*, 2002) the finding of this work from the impacted site disagree with this report but conforms with the result of the control site. Cu has the ability to complex with the organic matter through ion-exchange chelation. Phenolic and carbonyl functional groups helps in the bonding process (Mirillo *et al.*, 2002). The carbonate bound fractions recorded the least concentration of Cu from both impacted and control site. The Cu in the carbonate bound

phase is always not available because it is associated with humic substances which are high molecular weight substance with high stability (Vincente-Martorell *et al.*, 2009).

Arsenic

Arsenic distribution among the fractions from both sites does not follow a regular pattern. The order of distribution in the impacted site is F5>F1>F4>F3>F2 and F2>F5>F4>F1>F3 from the control site. Arsenic is significantly higher in the residual and exchangeable fraction and lower in carbonate bound and Fe-Mn oxide bound fractions of the impacted site, and significantly high in the carbonate bound and residual fractions and lower in exchangeable fraction and Fe-Mn oxide bound fractions of the control site. Alam *et al.* (2003), findings on high concentration of Arsenic in the residual fractions of soil sample agrees with this finding.

Cadmium

Cadmium distribution has regular pattern of mobility among the impacted and control site. The range of distribution is F5>F3>F2>F4>F1 for the impacted site and F5>F3>F2>F1>F4 for the control site. In this study, the residual and reduced fractions from both sites contained the higher concentration of Cd, but very minute concentration of Cd was observed in the exchangeable and carbonate fractions. The low concentration and mobility of Cd in the exchangeable and sorbed carbonate fractions is relative to the anthropogenic activities in the area (Iwegbue, 2011).

Chromium

Chromium has the least total concentration (1.64ppm) in all the fractions as compared to other metals. The distribution of Cr in the impacted and control site followed the same pattern of F5>F3>F4>F1>F2. The residual and reduced fractions showed higher concentration of Cr whereas the exchangeable and carbonate bound fractions has the least concentration. Ryan *et al.* (2002) reported that higher concentration of the Cr is found in the residual fraction. Iwegbue, (2011) reported that no Cr was found at the Carbonate bound fraction. The existence of chromium in the organic bound fraction is because of the formation of a stable complex with organic matter at the existing physico-chemical conditions (Kotokyl *et al.*, 2003).

IV. Conclusion

High level of heavy metals in the impacted area results in severe pollution of the entire Enyigba ecosystem, affecting both their water and crops since the soil serve as a reservoir for metals. Mn, Cr and Fe are present mainly in oxides, residual and organic forms; Cu occurs more in the oxides and residual fraction, while Zn, Cd, As and Pb mainly occurs in the residual forms. The total concentration of the bioavailable species (sum of the extractable and carbonate bounds), Pb, Zn, Mn, As, Cr and Cd are higher than the WHO permissible limit whereas Cu concentration is within the WHO permissible standard.

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