



Original Research Article

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ASSESSMENT OF HEAVY METALS CONTAMINATION IN SOILS IMPACTED BY MINING ACTIVITIES IN AKWANA, TARABA STATE, NIGERIA

B N Hikon^{1*}, G S Ngantem¹, G O Egah¹, D D Bwede²

1. Department of Chemical Sciences, Federal University Wukari,
P.M.B 1020 Wukari, Taraba State. Nigeria.

2. Department of Basic Science, College of Health Technology Zawan, Plateau State, Nigeria.

ABSTRACT: Sequential extraction was used to fractionate seven heavy metals (Pb, Ni, Zn, Cd, Cr, As and Hg) in soils from mining and control sites in Akwana and environs into five pools: exchangeable, carbonate, Fe-Mn oxide, organic and residual. AAS was used to analyze the samples. The percentage bioavailability of all the metals analyzed were higher than 50% in all the sites with the exception of Cr (49.50%) in the control site. This indicates that As, Ni, Hg and Pb are highly bioavailable and are known to be a cumulative poison in plants and mammals when its accumulation is above the threshold. Percentage bio availabilities of these seven heavy metals in the studied soils were in the order in the mining and control sites: As>Pb>Ni>Zn>Hg>Cr>Cd; Pb>Zn>>As>Hg>Ni>Cd>Cr. This indicates that lead and nickel had the highest chance of being accumulated. The enrichment Factor values for Pb, Ni, Zn, Cd, Cr, As and Hg were 1.488, 2.346, 1.056, 1.978, 1.222, 1.587 and 1.152 which indicates environmental pollution. Result obtained by spearman rank correlation coefficient, clearly shows that there is strong positive correlation ($\rho \approx 0.75$) between the concentration of heavy metals in the soil obtained from a mining and the control sites respectively. This implies that, as the concentration of the heavy metals increases in soil the more the rate at which plants absorb and store these metals.

KEYWORDS: soil, heavy metals, speciation and pollution.

Corresponding Author: B. N. Hikon*

Department of Chemical Sciences, Federal University Wukari, P.M.B 1020 Wukari,
Taraba State. Nigeria. Email Address: babahikon@fuwukari.edu.ng.

1. INTRODUCTION

Soils are the reservoir for many harmful constituents, elemental and biological, including heavy metals [11]. Heavy metals pollution has become a serious environmental concern everywhere due to the persistent and non-biodegradable properties of these contaminants. Soil and sediments serve as the ultimate sink of heavy metals in the marine environment and they play an important role in the transport and storage of potentially hazardous metals. The properties of metals in soils and sediments depend on the physiochemical form in which they occur [28]. Heavy metals are distributed throughout soil and sediment components and associated with them in various ways, including adsorption, ion exchange, precipitation and complexation and so on. Changes in environmental conditions, such as temperature, pH, redox potential and organic ligand concentrations can cause metals to be released from solid to liquid phase and sometimes cause contamination of surrounding waters in aquatic systems [33]. Heavy metals are found naturally in undisturbed soils and, in fact, small amounts of many metals are required by plants as micro and macronutrients to remain healthy [32, 30]. Heavy metals take part in biogeochemical cycles and are not permanently fixed in soils; therefore, assessment of their distribution in soils is a key issue in many environmental studies. [31]. Many soils are polluted with heavy metals due to the use of municipal compost, pesticides, fertilizers and emissions from municipal wastes incinerators, car exhausts, residues from metallic ferrous mines and smelting industries [34]. When soils are polluted with heavy metals, the question arises how large the risks for organisms or plants living on or in that soil will be. If the metal ions are attached to the soil particles they will not harm the plants and microorganisms that take up metals from the soil solution. For a metal pollution to be harmful to organisms requires certain level of exposure. Even when an organism is in full contact with the soil solution, not all metals in the soil solution attach to the organisms surface, which implies that exposure to a certain medium is not always equal to the level of exposure to the toxic metals. The chemical form in which metals occur in the solid and solution phase of the soil is called speciation [35]. Speciation analysis is an important present-day analytical tool particularly used for the elucidation of the chemical form(s) as well as the estimation of a specific metal when conducting toxicological and biochemical investigations. After years of considerable researches on metals pollution, it is now known that the distribution, mobility, bioavailability and toxicity of trace metals in environmental and biological systems depend not simply on their concentrations, but critically on their chemical forms [30]. Heavy metals in the soil from anthropogenic sources tend to be more mobile, hence bioavailable than pedogenic, or lithogenic ones [7]. Environmental pollution can be point source, non-point source (diffuse) pollution and natural or anthropogenic source pollution [13].

2. MATERIALS AND METHODS

The study area for this research work covered selected mining sites in Akwana district of Wukari Local Government area of Taraba State, Nigeria. Akwana lie between latitudes $7^{\circ} 51' 0''$ North and longitudes $9^{\circ} 14' 0''$ East and is 72Km away from Wukari which lie between longitudes $7^{\circ} 51' 0''$ North and $9^{\circ} 47' 0''$ East. The study also focused on less or non-polluted areas which act as control and is about 1.5Km away from the mining areas. The inhabitants use the areas for agricultural activities during the rainy and dry season [38]

Sample collection and preparation

Six (6) sampling spots were mapped out for soil samples collection at a distance of 50m from each other within the sampling sites (mining sites and control sites). 2kg of samples was taken using a clean stainless steel shovel from 0-15cm depth. The bulk samples of dried soil were collected and thoroughly mixed in a clean plastic container after which the sample were divided into four portions, samples were again taken from each portion and mixed thoroughly to obtain a representative sample. The homogenized soil sample were grounded with mortar and pestle, and sieved with 2mm mesh size, then stored in labeled polythene container prior to analysis. The soil samples was collected in the month of February, 2018.

All chemicals and reagents used for this research work are of analytical grade.

Determination of soil pH and temperature

The pH was measured in a 1:2.5 soil/H₂O suspension using a waterproof pH/ORP meter while the temperature probe was inserted into the soil solution and the reading was taken [39].

Total metal analysis

For each dried sieved soil sample 1.0g was weighed in to a 100cm³ beaker (pyrex), and digested with a mixture of 3cm³ concentrated HNO₃ and 2cm³ of HClO₄ for 1hour at 100°C in a fume cupboard. After cooling, the mixture was filtered and made up to 50cm³ volume with deionized water. It was analyzed using Atomic Absorption Spectrophotometer PG Instrument (AA-090M046) and the results reported in parts per million (ppm). Duplicate determinations were made [30].

Speciation of metals

Sequential extraction procedure (SEP) based on [30] adopted from [18] which defined the five geochemical forms of metals through a careful choice of extractants was used.

Soluble and exchangeable fraction (F1)

For each dried sieved soil sample, 1.0g was weighed and extracted with 20cm³ of a 1M MgCl₂ solution and adjusted to the pH of 7.0 and mechanically shaking for 1hour at 20°C in a polyethylene bottle. Then filtered into a 50cm³ volumetric flask and made up to 50cm³ with deionized water. It was analyzed using Atomic Absorption Spectrophotometer PG Instrument (AA-090M046) and the results reported in parts per million (ppm). Duplicate determinations were made.

Bound to carbonates fraction (F2)

The residues in F1 were extracted with 20 cm³ of a 1M CH₃COONa solution and adjusted to a pH of 5.0 with CH₃COOH by mechanical shaking for 4 hours at room temperature in a polyethylene bottle. The mixture was filtered and the filtrate made up to 50 cm³ volume with deionized water. This was then analyzed with Atomic Absorption Spectrophotometer PG Instrument (AA-090M046) and the results reported in parts per million (ppm). Duplicate determinations were made.

Bound to iron and manganese oxides fraction (F3)

Metals bound to iron and manganese oxides were extracted by pouring 50cm³ of a 0.04M NH₂OH.HCl and 10cm³ of 25% CH₃COOH onto the residue from F2 in a polyethene bottle and then heated for 6 hours at 96°C in a water bath. The mixture was filtered and the filtrate made up to 50cm³ volumetric flask with deionized water. This was then analyzed with Atomic Absorption Spectrophotometer PG Instrument (AA-090M046) and the results reported in parts per million (ppm). Duplicate determinations were made.

Bound to organic matter fraction (F4)

Metals bound to organic matter were extracted by pouring 15cm³ of a 0.02M HNO₃ and 25cm³ of a 30% H₂O₂ onto the residue from F3. The pH was adjusted to 2.0 with CH₃COOH and then heated for 5 hours at 85°C in a water bath. After cooling, 25cm³ mixture of 3.2M NH₄OAc and 20% HNO₃ in the ratio of 3:4 was added, followed by continuous shaking for 30 minutes at room temperature. The mixture was filtered and the filtrate made up to 50cm³ volumetric flask with deionized water. This was then analyzed with Atomic Absorption Spectrophotometer PG Instrument (AA-090M046) and the results reported in parts per million (ppm). Duplicate determinations were made.

Bound to the soil matrix or residual fraction (F5)

The residue from F4 was quantitatively transferred into 250cm³ beaker followed by the addition of 10cm³ mixture of analytical grade acids HNO₃: HClO₄ in the ratio 5:1. The digestion was performed at a temperature of about 190°C for 1.5 h in a fume cupboard. After cooling, it was filtered and the solution was made up to a final volume (50cm³) with deionized water in a volumetric flask. Atomic Absorption Spectrophotometer PG Instrument (AA-090M046) determined the metal concentrations. Duplicate determinations were made.

Determination of parameters

The data obtained from the experiment above was used to determine the following parameters:

- i. Statistical Analysis: The results of the analysis was subjected to statistical analysis using the spearman rank correlation coefficient ρ

$$\rho = 1 - \frac{6(\sum D^2)}{N(N^2-1)} \quad \text{Equ 1.}$$

Where, ρ = Spearman Rank Correlation Coefficient.

D = Difference in corresponding ranks.

N = Number of observation.

$$\text{ii. Percentage of heavy metals in the soil sample} = \frac{\text{concentration of metal specie}}{\text{total metal concentration}} \times 100. \text{ Equ. 2}$$

iii. Percentage bioavailable and non-bioavailable fractions:

$$\% \text{ bioavailability} = \frac{\text{exchangeable} + \text{carbonate} + \text{reducible}}{\text{exchangeable} + \text{carbonate} + \text{reducible} + \text{organic} + \text{residual}} \times 100. \text{ Equ 3}$$

$$\% \text{ non-bioavailability} = \frac{\text{organic} + \text{residual}}{\text{exchangeable} + \text{carbonate} + \text{reducible} + \text{organic} + \text{residual}} \times 100. \text{ Equ 4}$$

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[10]

$$\text{iv. Enrichment factor (EF)} = \frac{\text{concentration of metal in mining site}}{\text{concentration of metal in control site}} \text{ Equ. 5 [14]}$$

3. RESULTS AND DISCUSSION

The result of the soil pH obtained from the mining and control sites were 7.80 and 6.20 respectively. This showed that the mining site was slightly alkaline while that of the control was slightly acidic. Soil temperatures were within the range of 28 to 29.5⁰C, which is moderately effective and suitable for plants growth, this agreed with what [1] reported earlier in their work.

Table 1: Temperature and pH of Soil Samples

Samples	Temperature ⁰ C	pH
Soil _M	28	7.80
Control	29.5	6.20

Soil_M = Soil from Mining Site.

The total metal concentration of soil taken from the mining and control sites were showed in Table 2 below. The concentration of heavy metals determined were within the maximum permissible limits of soil except for Arsenic sample in the mining site that is above the permissible limits [2].

Table 2: Total Metal Concentration in the Soil Samples (mg/kg)

Heavy metal	Soil _M	Control	USEPA (2002)
Pb	2.562±0.001	1.722±0.001	400
Ni	0.298±0.002	0.127±0.002	140
Zn	1.522±0.002	1.441±0.001	2, 200
Cr	0.273±0.001	0.138±0.004	36
Cd	0.220±0.020	0.180±0.002	0.86
As	0.235±0.003	0.148±0.003	0.21
Hg	0.106±0.005	0.092±0.001	-

Soil_M = Soil from Mining Site.

[3, 4] reported in their work that in aqueous environment, the inorganic arsenic species; Arsenite [As (III)] and Arsenate [As (V)] are the most abundant species and their transport is aided by competitive adsorption, an alkaline pH and suboxic aqueous environment. The high concentration of Arsenic could be attributed to the mining activities, transport mechanism, which includes agricultural activities such as application of agrochemicals and atmospheric depositions on the site. This is in agreement with the work reported by [5]. Similarly, the concentration of the metals in soil samples obtained from the mining site are significantly higher than their corresponding levels in the control samples. This agreed with the work of [6] who reported that, the high level of heavy metals in soil is associated with anthropogenic activities. Heavy metals in the soil from anthropogenic sources tend to be more mobile, hence bioavailable than pedogenic, or lithogenic ones [7]. Zn present in the area could be as a result of its natural abundance and its association with Cadmium as a result of mechanical abrasion of crushing/grinding [8]. This study agreed with the report of [36], that Zn is associated with Fe-Mn oxide phase because of the high stability constant of Zn oxides. Iron oxides adsorb considerable quantities of Zn, and this oxide may also occlude Zn in the lattice structure. The result of speciation studies conducted from the soil obtained from the mining site and the one obtained from the control site is presented in Table 3 below.

Table 3: Heavy Metal Speciation in Soil Samples

Metals	Pb	Ni	Zn	Cr	Cd	As	Hg
Exchangeable							
fraction							
Samples							
X	0.892±0.002	0.071±0.002	ND	ND	0.022±0.016	0.702±0.008	0.086±0.005
Y	0.073±0.001	0.003±0.001	0.113±0.002	ND	0.016±0.005	0.399±0.006	0.072±0.003
Carbonate							
Fraction							
Samples							
X	0.729±0.003	0.040±0.001	0.256±0.001	0.040±0.002	0.022±0.003	0.142±0.006	0.086±0.002
Y	0.096±0.004	ND	0.385±0.007	0.020±0.004	0.019±0.001	ND	0.073±0.001
Reducible							
fraction							
Samples							
X	0.029±0.001	0.040±0.001	0.405±0.001	0.0500±0.002	0.018±0.003	ND	0.065±0.001
Y	0.117±0.006	0.072±0.001	0.447±0.005	ND	0.019±0.002	0.399±0.025	0.068±0.002
Oxidizable							
Fraction							
Sample							
X	0.414±0.005	0.090±0.002	0.264±0.030	0.030±0.004	0.024±0.001	ND	0.092±0.008
Y	1.144±0.025	0.018±0.001	0.210±0.008	0.020±0.002	0.024±0.002	ND	0.089±0.006
Residual							

Sample	Fraction						
X	0.274±0.050	0.048±0.002	0.438±0.025	0.020±0.001	0.027±0.004	0.089±0.002	0.081±0.002
Y	0.127±0.008	0.012±0.003	0.191±0.050	0.089±0.007	0.023±0.003	0.297±0.001	0.079±0.004

X = Mining Soil, Y = Control

Speciation of metals is a useful tool normally used to know the concentration of pollutants in various fractions of soil samples. It gives an estimate amount of the metals available to ecological materials. The amount of any metal concentration depicts the toxicity level for the metal [5]. The five geochemical forms F1-F5, where F1= exchangeable fraction, F2 = carbonate fraction, F3 = reducible fraction, F4 = organic fraction, F5 = residual fraction of metals are operationally defined by careful sequential fractionation order that follows a decreasing solubility and increasing strength of extractants [9]. Irrespective of sampling site, the distribution of metals in soil samples generally followed the order below for the various metals studied:

Pb: exchangeable > carbonate > organic > residual > reducible.

Ni: reducible > residual > organic > exchangeable > carbonate.

Zn: reducible > residual > carbonate > organic > exchangeable.

Cr: residual > exchangeable > organic > reducible.

Cd: residual > organic > carbonate > reducible > exchangeable.

As: exchangeable > reducible > residual > carbonate.

Hg: residual > organic > exchangeable > carbonate > reducible.

The results indicate that all the metals analyzed in soils obtained from the mining and control site were associated with the residual fraction (F4) followed by the reducible fractions F3 at varied concentration. Arsenic concentrations in the organic fraction (F5) of both samples were not detected. The highest concentration of Cr, Cd and Hg were found in the residual and organic fractions. This result agreed with the work of [12] who reported that the greatest percentage of Cr, Cd and Hg are in the residual and organic phases while Zn is found more in the residual and reducible phases. This disagreed with the work earlier reported by [10] that most metals are associated with exchangeable and organic phase. The residual phase represent metals largely embedded in the crystal lattice of the soil fraction and should not be available for remobilization except under very harsh conditions [15]. The carbonate fraction is influenced by pH, and the observed pH of the soils at both sites is in the ranged 6.20-7.80. This agreed with the report of [37] that at low pH, H⁺ (H₃O⁺) occupies more adsorption sites which results in carbonate-bound, heavy metals precipitated more easily than at higher pH values. The heavy metal release rates were affected to a much greater extent in the low pH (4-7) condition than in high pH (8-10) condition.

Table 4: Percentage (%) of Heavy Metals in Soil

Fractions	Samples	Pb	Ni	Zn	Cr	Cd	As	Hg
Exchangeable	X	23.10	19.46	26.61	14.65	10.91	26.38	16.22
	Y	04.29	02.36	07.84	14.49	08.89	20.27	15.65
Carbonate	X	19.47	13.42	16.82	ND	10.00	08.51	16.22
	Y	05.57	ND	26.72	ND	10.56	ND	15.80
Reducible	X	01.13	13.42	26.61	18.32	08.18	ND	12.22
	Y	05.57	28.35	31.02	ND	10.56	20.27	15.65
Organic	X	21.13	30.20	17.35	14.65	10.91	ND	17.29
	Y	33.22	14.17	14.57	14.49	13.33	ND	19.26
Residual	X	10.69	16.11	28.78	18.32	12.27	06.38	15.09
	Y	07.36	09.45	13.25	32.25	12.78	09.46	17.17

X = Mining Soil, Y = Control, ND = Not Detected.

The result of percentage of heavy metals in the study areas is presented in Table 4 above. From the result above, the percentage of Pb, Ni, Zn, Cr, Cd, As and Hg constitute only 06.79 - 26.72% in the carbonate fractions. The metals As is distributed more as soluble and exchangeable, carbonate, Fe-Mn oxides and as residual. Arsenic, seemed to be the most mobile and available metal, approximately 26.38; 20.27% in the mining and control site. The residual and exchangeable fractions have the highest percentage. The percentage from residual fraction varies from 06.79 - 28.78% in the soil. The results of this study agreed with the findings of [18] who revealed that Cd, Zn, and Ni were strongly associated in residual fractions. A similar result was reported by [16] who revealed that around 90% of Cd, Zn, Ni were associated with the residual fractions. The result of Pb in this work is in agreement with the findings of [17] that there was mobility in all the fractions: exchangeable and specifically adsorbed fraction, reducible fraction, and oxidizable fraction. There are also average percentage abundances of most metals found in the reducible phase, Ni and Zn. Metals in this fraction are bound to oxides of Fe and Mn in soil. It is well established that Fe and Mn oxides exist as nodules, concretions or cement between particles, or simply as coating on particles. These oxides are excellent scavengers for heavy metals and are thermodynamically unstable under anoxic conditions (presence of oxygen), hence, changes of anoxic conditions of the soil will either influence the release or retention of elements in the reducible phase. Under reduced-alkaline conditions, the reducible fraction was affected, but the oxidizable fraction was slightly favored. Both pH and redox potential Eh are the main factors that control the release of metals [18, 19]. The relative percentage abundance exhibited by metals in the oxidizable phase (organic-bound phase) could be attributed to the organic matter load of soil. The moderately high percentage of the organic bound fraction indicates the strong ability of the heavy metal to form complexes with organic matter thereby reducing its mobility and phytotoxicity

[21, 20]. The percentage of metals extracted in residual fraction for Cd, Ni and Pb in both sample sites follows this trend Ni > Cd > Pb. This result agrees with the work of [22] who reported that Cd, Ni and Pb were mostly associated with the residual phase. Metals concentrations in association with carbonate fraction are the least in all cases studied. The concentration of metals in this fraction is in agreement with the work reported by [23] which showed only relatively lower amount of Cd, Cr, Pb and Zn in the carbonate fraction.

Table 5: Percentage Bioavailable and Non-bioavailable Fractions

Samples	Fractions	Pb	Ni	Zn	Cr	Cd	As	Hg
X	Bioavailable	69.96	63.89	60.29	54.26	53.47	84.54	58.02
	Non-bioavailable	30.04	36.11	39.71	45.74	46.53	15.46	41.98
Y	Bioavailable	71.40	56.52	70.21	49.50	54.87	68.18	56.58
	Non-bioavailable	28.60	43.48	29.79	50.50	45.13	31.82	43.42

X = Mining site, Y= Control site.

The comparative bioavailability levels of metals in each site are presented in Table 5. The fate of a metal in an environment is determined by the ease of availability, the higher the level of bioavailability, the higher the impact on the target system. The ease of extraction is related to the degree of solubility and bioavailability of metal form. The value of MBF for elements provides information about their potential mobility in soils and availability to plants [15]. The value of MBF less than 50% for any element indicates that this element is immobile and unavailable for plants. However, the value of MBF up to 50% or greater than 50 % for a particular metal suggests that this element is highly mobile and available for plants [24, 25]. The percentage bioavailability of all the metals analyzed were higher than 50% and above in all the sites with the exception of Cr (49.50%) in the control site. This indicates that the metals are mobile and hence bioavailable to plants. However, As, Pb, Ni, and Zn contribute highest to the bioavailable content, a greater percentage (>60%) was found in the bioavailable form. This suggests that As, Ni, Hg and Pb are highly bioavailable and are known to be a cumulative poison in mammals when its accumulation is above the threshold [26]. The result showed that the percentage bioavailability of Cadmium in the control site was 54.87% (slightly acidic soil) and higher than that of the mining site which was 53.47% (slightly alkaline) as shown in Tables 1 and 4. This agrees with the report of [27] that in soil, the chemistry of cadmium is largely controlled by pH. Cadmium bioavailability is higher in acidic soils, and lower in chalky/lime soils. Under acidic conditions, cadmium solubility increases, and very little adsorption of cadmium by soil colloids, hydrous oxides, and organic matter takes place. Both toxicity and bioavailability of cadmium are influenced by soil characteristics. Cadmium enters agricultural soils from the atmosphere and from application of phosphate fertilizers and sewage sludge. The high percentage bioavailability of mercury obtained in this work

(58.02; 50.88%) agreed with the reports of [29], that mercury occurred mainly as organic and inorganic mercury which have accumulated in the environment, especially in soils and oceans, as a result of these past emissions and releases from human activities. Although mercury pollution can occur naturally in the environment through events such as forest fires and burning of fossil fuels, cement production, mining and smelting, and small-scale gold mining are some of the activities emitting mercury which can build up in soils.

Table 6: Spearman Rank Correlation Coefficient (ρ) of soil obtained from Mining and Control Sites

Metals	Soil (x)	Control (y)	Rank (x)	Rank (y)	D	D2
Pb	2.563	1.722	1	1	1	1
Ni	0.298	0.127	5	7	-2	4
Zn	1.522	1.441	3	2	1	1
Cr	0.273	0.138	6	6	0	0
Cd	0.220	0.180	7	5	2	4
As	0.235	0.148	1	3	-2	4
Hg	0.106	0.092	4	4	0	0
Total	14					

$$\rho \approx 0.75$$

From the results of the analyses obtained above, there is a strong positive correlation between the soil obtained from the mining sites and the control sites ($\rho \approx 0.75$). This indicates that, as the concentration of heavy metals in the mining sites increases, the control site also increases and the more the rate at which plants absorb and store these metals.

Table 7: Enrichment Factor (EF)

Heavy metal	EFSOIL
Pb	1.488
Ni	2.346
Zn	1.056
Cr	1.978
Cd	1.222
As	1.587
Hg	1.152

EF = Enrichment Factor

The Enrichment Factor (EF) was calculated for the seven metals (Pb, Ni, Zn, Cr, Cd, As and Hg) obtained from the study areas to establish the degree of soil contamination and heavy metal accumulation. It is the ratio between the concentration of metals in contaminated soil and the concentration of metals in uncontaminated (control) soils. Values greater than 1 indicate

environmental pollution [14]. Their respective EF values were 1.488, 2.346, 1.056, 1.978, 1.222, 1.587 and 1.152 for Pb, Ni, Zn, Cr, Cd, As and Hg. For the seven metals studied, the EF values are far above the value of contamination resulting in high availability and distribution of metals in the soils. Their high EF values are attributed to the mining and smelting activities taken place in the study area. These values may be an indication that there may ultimately be an increase in metal accumulation in plants located on the sites. The result of this study shows that Zn contaminant is very low or negligible. Hg and Cd are moderate contaminants while Pb, As, Cr and Ni are the most contaminants in the study area.

4. CONCLUSION

The results of the analysis of this research work showed that both the mining and control sites in Akwana and environs contained certain concentration of heavy metals in different fractions and the total metal concentration of Pb, Ni, Zn, Cr, Cd, As and Hg were also determined. There is a strong positive correlation between the soil obtained from the mining and control sites and the percentage bioavailability of almost all the heavy metals are greater than 50%. This indicates that the metals are mobile and bioavailable for plant uptake. Mining activities contaminate soil, hence all the sample areas are contaminated as indicated by the enrichment factor.

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CONFLICT OF INTEREST

There are no conflict of interest, financial or otherwise.

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