International Journal of Modern Chemistry, 2018, 10(2): 154-171

Modern Scientific Press

International Journal of Modern Chemistry **ISSN: 2165-0128**

Journal homepage: www.ModernScientificPress.com/Journals/IJMChem.aspx *Florida, USA*

Article

Bioavailability and Plants Uptake of Selected Heavy Metals (Pb, Zn, Cr, Cd, Ni, As and Hg) in Akwana Mining Sites and Environs, Wukari, Taraba State. Nigeria

B. N. Hikon[1,*], G. O. Egah[1], G. S. Ngantem[1], and D. D Bwede[2]

[1]*Department of Chemical Sciences, Federal University Wukari, PMB 1020, Taraba State, Nigeria*

[2]*Chemistry Department University of Agriculture, Makurdi. Benue State*

* Author to whom correspondence should be addressed; E-Mail: babahikon@fuwukari.edu.ng

Article history: Received 1 June 2018, Revised 8 July 2018, Accepted 15 July 2018, Published 19 July 2018.

Abstract: The concentration of heavy metals determined were within the maximum permissible limits of soil except for Arsenic in the mining site that is slightly above the permissible limits (0.21mg/kg). This could be attributed to the mining activities, transport mechanism, agricultural activities and atmospheric depositions on the site. 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. From the results of this analyses, there is a strong positive correlation ($\rho \approx 0.93$) between the plants and soil obtained from the mining sites, also a strong positive correlation between the maize grains obtained from the mining and control sites ($\rho \approx 0.84$) and between the maize grains and soil obtained from the control site ($\rho \approx 0.61$). This indicates that as the concentration of the heavy metals increases in soil the more the rate at which plants absorb and store these metals. The transfer factors (tf) for the metal in the soil obtained from the mining site were significantly different from those for control site and according to the type of plants. The highest transfer factor values are 0.171; 0.097, 0.161; 0.102, 0.032; 0.029 and 0.096; 0.054 for Zn, Cd, As and Hg in the maize grains obtained from the mining and control site, though less than unity, (this implies that the concentrations of heavy metals in plants are less than the concentration in soils) but the

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

concentration of Pb, Cd, As and Hg in maize grains grown in the mining site were found to be higher and slightly above the permissible limit (0.01, 0.01, 0.01 and 0.001mg/kg).

Keywords: bioavailability, heavy metals, soil and transfer factor

1. Introduction

The chemical form in which metals occur in the solid and solution phase of the soil is called speciation. Speciation analysis is an important present-day analytical tool particularly used for the elucidation of the chemical form(s) as well as the quantitative estimation of a specific element when conducting toxicological and biochemical investigations [27]. Bioavailability is the fraction of the total amount of a metal in a specific environmental compartment that, within a given time span, is either available or can be made available for uptake by microorganisms from the direct surrounding of the organism [26]. The free metal ion concentration is, in most cases, the key factor in predicting bioavailability [35]. The heavy metals accumulation in plants highly depends on the availability in the soil [6]. The higher the amount of heavy metals in the soil, the higher the tendency of accumulation in plants tissues [10].

It has been widely accepted that soil plays a key role in sustaining life in earth's ecosystems [48]. The very survival of mankind is tied on its productivity as a medium for plants to grow [17]. Soil consists of a heterogeneous media comprised of decomposed rock fragments, clay minerals, and oxides of Fe, Al and Mn, organic materials, organo-metallic complexes and soil solutions [5]. However, soil is also a transmitter of many pollutants including potentially toxic metals into the atmosphere, biosphere and water resources [8]. Heavy metals in soil exist in several different forms and are associated with a range of other components [37]. The accumulation of metals in soil, particularly Pb, Cd, Cu, Ni, Cr and Zn is of concern [24, 25, 36, 50]. Heavy metals emanating from anthropogenic sources are more dangerous because of their instability and solubility leading to high bioavailability [11, 4]. Their form can strongly influence their speciation and availability the plants [44]. They can also transform to other species and easily accumulate to toxic levels in the topsoil [21] because of their non-biodegradable nature [34]. At toxic levels they affect biogeochemical cycles and accumulate within living organisms and eventually make their way to humans through the food chain, where they can cause perturbation to biological reactions [13, 32, 333, 40]. Further, the few studies that have been done report total concentration of the heavy metals [32] present and not their form thus providing limited information about the potential toxic behavior, mobility, bioavailability and environmental safety [51]. Therefore, it is necessary to determine

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

the forms they exist and the concentration levels in each form. This will provide predictive insights on the bioavailability, mobility and fate of heavy metal contaminants [52, 53]. The chemical form or species of the heavy metal is a crucial factor in assessing their impacts on the environment because it controls its bioavailability or mobility. In recent years there has been increased interest in the studies on speciation or chemical forms of heavy metals in polluted soils and sediments using sequential extraction techniques because these provide knowledge on metal affinity to soil components and the strength with which they are bound to matrix [54]. The use of sequential extractions, although time consuming, furnishes detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of trace metals [55, 56]. Sequential extraction procedures selectively extract metals bound by specific soil fractions with minimal effects on the soil components [57].

Plants absorb metals from soil and water, they predominantly accumulate in the roots, and then some portions are transfer to parts of plant. Plant can immobilize heavy metals through absorption and accumulation by roots, adsorption onto rots, or precipitation within rhizosphere [47]. Heavy element uptake by plants is generally the first step of their entry into the agricultural food chain [18]. Plant species and relative abundance and availability of necessary elements also control metal uptake rates. Heavy metals are persistent in nature, hence became accumulated in soil and plants. Exposure of plants to non-redox reactive metals results in oxidative stress as indicated by liquid peroxidation, H_2O_2 accumulation and an oxidative burst [34]. Generally, plants show signs of stress when they accumulate high percentage of heavy metals [23]. In heavy metals polluted soils, plants growth can be inhibited by metal absorption [12]. Roots crops like potatoes and carrots, leafy vegetables like spinach and lettuce and parts of plants that are grow near the soil are at greater risk for exposure to metal contamination than the higher portions of plants, like fruits or berries [23]. Plants are known to take up and accumulate heavy metals from contaminated soil and sediments with variations in metal content dependent on several factors such as soil properties, plant species, plant age, and time interval of metallic soil input, nutrient availability and interaction among the metals [29].

2. Materials and Method

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^o 51’ 0”North and longitudes 9^o 14’ 0”East and is 72 Km away from Wukari which lie between longitudes 7^o 51’ 0” North and 9^o 47’ 0” East. The study also focused on less or non-polluted areas which act as control and is about 1.5 Km away from the mining areas. The inhabitants use the areas for agricultural activities during the rainy and dry season.

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

2.1. Collection and Preparation of Plants Sample

A 2.0 kg of Edible plant (maize grains) samples grown on the farms around the mining sites and those grown around their homes (control) were randomly collected. A total of ten (10) plants **s**amples were collected randomly from the two study areas, six (6) from the mining sites and four (4) from the control site. The plant samples were mixed to give the representative fraction of each of the plant. The harvested maize were threshed manually to obtained the grain and oven dried at 70 °C until stable weights were obtained. It was then grounded in a mortar and sieved with 2 mm mesh size, then stored in labeled polythene container prior to analysis. The samples were collected in the month of August, 2016.

2.2. Collection and Preparation of Soils Sample

A total of ten (10) sampling spots were randomly mapped out for soil samples collection at a distance of 50 m from each other within the sampling sites (six spots from mining sites and four control sites). 1 kg of samples was taken using a clean stainless steel shovel from 0-15 cm depth. The soil sample was oven dried at 85ºC. The bulk samples of dried soil were 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 2 mm mesh size, then stored in labeled polythene container prior to analysis. The samples were collected in the month of August, 2016.

A 1.0 g of the powdered maize plant samples was digested with 10 cm^3 mixture of analytical grade acids HNO_3: $HCIO_4$ in the ratio 5:1. The digestion was performed at a temperature of about 90 ºC for 30 minutes in a fume cupboard until clear solutions were obtained. Digested samples were allowed to cooled, filtered into a 100 cm^3 volumetric flask, and made up to the mark with deionized water. Atomic Absorption Spectrophotometer Model, AA090M046 PG Instruments was used determine trace metals concentration in the samples. Triplicate determinations were made.

2.3. Determination of Soil pH and Temperature

About 1.0 g of dried soil sample from each sites were mixed with 20 cm^3 of deionized water in a 50 cm^3 beaker and stirred with a glass rod. The pH and temperature was measured by introducing a glass probe of the pH meter and temperature probe into the soil solution and the reading was taken.

2.4. Total Metal Analysis in Soil

For each dried sieved soil sample 1.0 g was weighed in to a 100 cm^3 beaker (pyrex), and digested with a mixture of 3 cm^3 concentrated HNO_3 and 2 cm^3 of $HClO_4$ for 1hour at 100 ºC in a fume cupboard. After cooling, the mixture was filtered and made up to 50 cm^3 volume with deionized water. It was

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

analyzed using Atomic Absorption Spectrophotometer Model, AA090M046 PG Instruments and the results reported in parts per million (ppm). Triplicate determinations were made.

2.5. Speciation of Metals

Heavy metals in the soil were extracted using the Sequential extraction procedure (SEP) based on Adriano, [4] adopted from [39] which defined the five geochemical forms of metals through a careful choice of extractants was used.

The exchangeable fractions (F1), was extracted by shaking about 1.0 g soil sample in 20 cm^3 of a 1M $MgCl_2$ solution and adjusted to the pH of 7.0 using mechanical shaker for 1hour at 20^oC in a polyethylene bottle. The mixture was filtered into a 50 cm^3 volumetric flask and made up to 50 cm^3 with deionized water. The carbonate fractions (F2), were extracted with 20 cm^3 of a 1M CH_3COONa solution and adjusted to a pH of 5.0 with CH_3COOH and mechanically shaking for 4 hours at room temperature in a polyethylene bottle. The mixture was filtered and the filtrate made up to 50 cm^3 volume with deionized water. The metals bound to iron and manganese oxides reducible fractions, F3) were extracted by pouring 50 cm^3 of a 0.04M $NH_2OH.HCl$ and 10 cm^3 of 25 % CH_3COOH onto the residue from F2 in a polythenes bottle and then heated for 6 hours at 96 ^oC in a water bath. The mixture was filtered and the filtrate made up to 50 cm^3 volumetric flask with deionized water. Metals bound to organic matter (oxidizable fraction, F4) were extracted by pouring 15 cm^3 of a 0.02M HNO_3 and 25 cm^3 of a 30 % H_2O_2 onto the residue from F3. The pH was adjusted to 2.0 with CH_3COOH and then heated for 5 hours at 85 ^0C in a water bath. After cooling, 25 cm^3 mixture of 3.2M NH_4OAc and 20 % HNO_3 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 50cm^3 volumetric flask with deionized water. The residual fractions (F5), the residue from F4 was quantitatively transferred into 250 cm^3 beaker followed by the addition of 10 cm^3 mixture of analytical grade acids HNO_3:$HCIO_4$ in the ratio 5:1. The digestion was performed at a temperature of about 190 ^oC for 1.5 h in a fume cupboard. After cooling, it was filtered and the solution was made up to a final volume (50 cm^3) with deionized water in a volumetric flask. Atomic Absorption Spectrophotometer Model, AA090M046 PG Instruments was used to determine the metal concentrations for all the filtrates. Triplicate determinations were made. All chemicals and reagents used for this research work are of analytical grade from sigma and BDH Company.

2.6. Percentage Bioavailable and Non-bioavailable Fractions

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. [3] Reported that the ease of extraction is related to the degree of solubility and bioavailability of metal form. Therefore, the metal percentage

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

bioavailability factor (MBF) is

$$(\%)\ \text{Bioavailability} = \frac{Exchangeable + Carbonate + \text{Re}\,ducible}{Exchangeable + Carbonate + \text{Re}\,ducible + Organic + \text{Re}\,sidual} \times 100 \qquad (1)$$

$$(\%)\ \text{Non-bioavailability} = \frac{Organic + \text{Re}\,sidual}{Exchangeable + Carbonate + \text{Re}\,ducibl + Organic + \text{Re}\,sidual} \times 100 \qquad (2)$$

The operational fractions whose conditions are not easily attainable in the geochemical conditions of the soil are regarded as non-bioavailable fractions (NBF). The value of MBF for elements provides information about their potential mobility in soils and availability to plants [49]. The value of MBF up to 10% for any element indicates that this element is immobile and unavailable for plants [32].

2.7. Transfer factor

The Transfer factor (tf) is a competent technique developed to assess the level of the metal in the plant as a fraction of the soils total. Previous studies have indicated that the uptake of metals by plants differs from one metal to another, from one plant species to another and from one polluted soil to the other [58].

$$\text{Transfer factor (TF)} = \frac{Concentration\,in\,plant\,tissue}{Concentration\,in\,soils\,ampl} \qquad (3)$$

2.8. Data Analysis

In order to study the level of the soils contamination and absorption by plants, the results of concentrations of heavy metals in the soils and plants were subjected to correlation analysis to determine association as well as the differences in the concentrations between different sampled. Descriptive statistical analysis was also employed for the data obtained. Mean and standard deviations were determined.

3. Results and Discussion

The result of the pH obtained from the analysis of the soil samples from the study areas are presented in Table 1. The pH were determined by using Hanna Instrument, portable pH meter model HI8043. The pH of soil obtained from the mining site and the control site were 7.80 and 6.20 respectively. The result of this studied showed that the soil obtained from the mining site is slightly alkaline while that of the control is slightly acidic. Soil temperature was within the range of 28 to 29 ºC, which is moderately effective and suitable for plants growth, this agreed with what [15] reported earlier in their work.

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

Table 1: Temperature and pH of Soil Samples

Samples	Temperature ^{o}C	pH
$Soil_P$	29	7.80
Control	28	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 2.0. The concentration of heavy metals determined were within the maximum permissible limits of soil except for Arsenic in the mining site that is slightly above the permissible limits (0.21 mg/kg) [1]. This could be attributed to the mining activities, transport mechanism, which includes contamination through runoff water, agricultural activities, which includes application of agrochemicals such as fertilizers (manure) and pesticides, herbicides and atmospheric depositions on the site. This is in agreement with the work reported by [9].

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

Similarly, the concentration of the metals in soil samples obtained from the mining and control site are significantly higher than their corresponding levels in the control samples. This could be attributed to possible pollution of the sample areas, due to excessive usage of fertilizers, herbicides and other agrochemicals as well as the use of wastewater in irrigating the soils and the environmental factors pertinent in the study area. This agreed with the work of [43] who reported that, the high level of heavy metals in soil is associated with anthropogenic activities.

Zn presents in the area could be as a result of its natural abundance, its association with Cadmium and as a result of mechanical abrasion of crushing/grinding [30]. This study agreed with the report of [7],

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

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 percentage of Pb, Ni, Zn, Cr, Cd, As and Hg for the study area contribute only about 06.79-26.72 % in the carbonate fractions. Arsenic is distributed more as soluble and exchangeable, carbonate, Fe-Mn oxides and as residual. Arsenic, As seemed to be the most mobile and available metal, approximately 26.38; 17.02 % (figure 1 and 2). The higher percentages of metals were from residual and exchangeable fractions. The percentage from residual fraction varies from 06.79-28.78 % in the soil (figure 1 and 2). The results of this study agreed with the findings of [39] who revealed that Cd, Zn, and Ni were strongly associated in residual fractions. A similar result was reported by [19] who revealed that around 90 % of Cd, Zn, Ni were associated with the residual fractions.

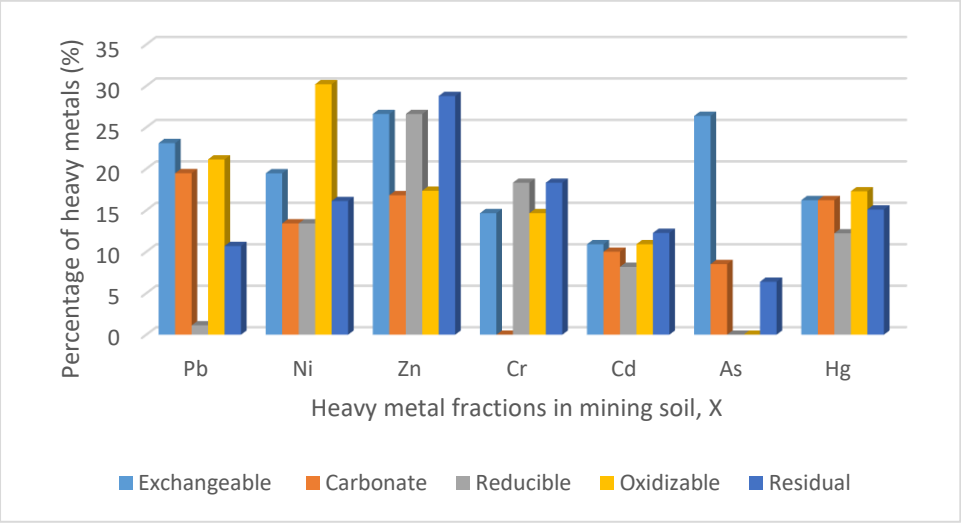

Figure 1: Percentage of heavy metals speciation in the mining soil, X

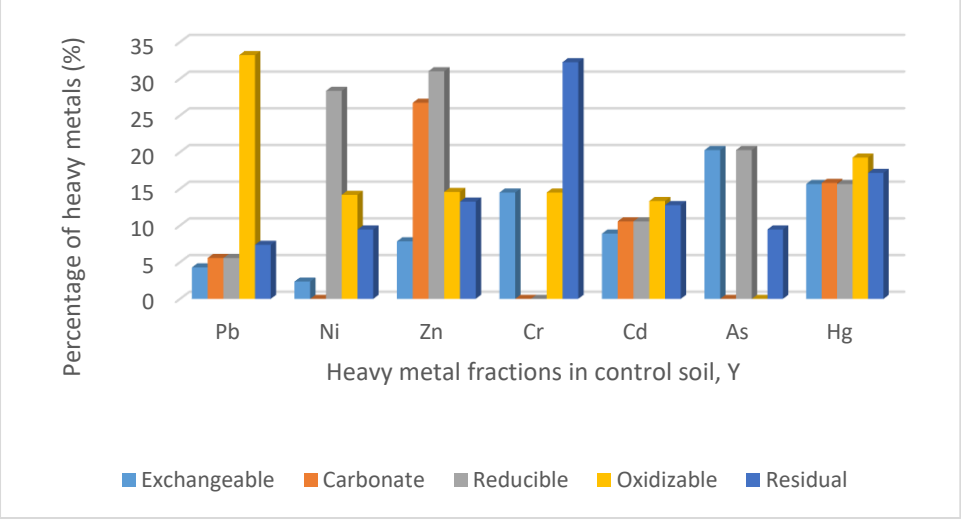

Figure 2: Percentage of heavy metals speciation in the control soil, Y

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

The result of Pb in this work is in agreement with the findings of [38] 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 (figure 1 and 2). 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 [39, 14].

The relative percentage abundance exhibited by metals in the oxidizable phase (organic-bound phase) could be attributed to the organic matter load of soil. On the other hand, it may be due partly to the variations from different agricultural practices and application of agrochemicals on the farmlands around the sampling locations. The anthropogenic inputs (human activities) differ from one location to the other. About 10.64; 16.78 % of Pb, 10.06; 14.17 % of Ni and 12.26; 10.87 % of Hg were found in the oxidazable fraction. 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 phytoxicity [27, 8]. 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 Ramirez et al [31] 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 areas. The concentration of metals in this fraction is in agreement with the work reported by [2] which showed only relatively lower amount of Cd, Cr, Pb and Zn in the carbonate fraction.

The comparative bioavailability levels of metals in each site are presented in Table 3. 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 operational fractions whose conditions are not easily attainable in the geochemical conditions of the soil are regarded as non-bioavailable fractions (NBF). The value of MBF for elements provides information about their potential mobility in soils and availability to plants [49]. The value of MBF up to 10% for any element indicates that this element is immobile and unavailable for plants [32]. In addition to that, the value of MBF up to 50 % or greater than 50 % for a particular element suggests that this element is highly mobile and available for plants [28].

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

Table 3: Percentage Bioavailable and Non-bioavailable Fractions

Samples	Metals	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 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. Heavy metals in the soil from anthropogenic sources tend to be more mobile, hence bioavailable than pedogenic, or lithogenic ones [16]. 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 [41]. The concentrations of metals in maize (grains) grown in mining and control site are shown in Table 4. The concentration of Pb, Cd, As and Hg in maize grains grown in the mining site were found to be higher and above the permissible limit [46] and [42] while Zn, Cr and Ni are within the permissible limits. This high concentration of the metals could be as a result of mining activities, discharged, mechanical wears from crushing machines in the mining site and runoff water that contain these metals. The concentration of Pb, Ni, Zn, Cr, and Cd in maize obtained from the control site were within the permissible limits for grains while the concentration of As and Hg were above the permissible limits but lower than those in the mining site. This study revealed that maize grown around the mining site were highly contaminated compared to those from the control. The results of the analyses showed that heavy metals are easily accumulated in grains and this agreed with the finding of [22].

The Transfer factor (tf) is a competent technique developed to assess the level of the metal in the plant as a fraction of the soils total. Previous studies have indicated that the uptake of metals by plants differs from one metal to another, from one plant species to another and from one polluted soil to the other [6]. The results from this studied as shown in Table 5 indicates that the uptake of each metal differs from one soil site to another and from one plant to the other.

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

Table 4: Total Metal Concentration in Plant Samples (mg/kg)

Heavy Metals	Maize $_M$	Control	WHO (2011)	USEPA (2006)
Pb	0.020±0.003	0.013±0.002	0.01	0.015
Ni	0.048±0.001	0.013±0.001	0.07	0.05
Zn	0.260±0.002	0.114±0.001	5.00	5.00
Cr	0.02±0.001	0.01±0.001	0.05	0.10
Cd	0.016±0.001	0.014±0.002	0.01	0.005
As	0.093±0.003	0.065±0.001	0.01	0.01
Hg	0.051±0.001	0.010±0.002	0.001	0.002

$Maize_M$ = Soil from Mining Site

Table 5: Transfer Factor (TF) of Heavy Metals from Soil to Plants.

Heavy metal	TF_{MM}	TF_{MC}
Pb	0.008	0.008
Ni	0.045	0.022
Zn	0.171	0.097
Cr	0.007	0.007
Cd	0.161	0.102
As	0.032	0.029
Hg	0.096	0.054

TF_{MM} = Transfer Factor in maize from mining site, TF_{MC} = Control.

This variation might be explained in terms of the available salts ions present in the soil, which differ from one soil to the other. The transfer factors (tf) for the metal in the soil obtained from the mining site were significantly different from those for control site and according to the type of plants. Highest transfer factor values (0.171; 0.097, 0.161; 0.102, 0.032; 0.029 and 0.096; 0.054) were obtained for Zn, Cd, As and Hg in the maize grains obtained from the mining and control site though less than unity, (this implies that the concentrations of heavy metals in plants are less than the concentration in soils). One of the reasons for these results is that Cd occurs with Zn in nature and are more mobile in nature [20]. The rate of metal uptake by the plant could have been affected by the other factors such as plant age, plant species, soil pH, nature of soil and climate [47].

The results of this analyses was subjected to spearman correlation coefficient as shown in table 6-8, indicates that there is a very strong positive correlation ($\rho \approx 0.93$) between the maize grains and

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

soil obtained from the mining sites, also a strong positive correlation between the maize grains and soil obtained from the control sites ($\rho \approx 0.61$). The maize grains obtained from the mining and control sites shows a strong positive correlation ($\rho \approx 0.84$). This indicates that as the concentration of the heavy metals increases in soil the more the rate at which plants absorb and store these metals.

Table 6.0: Spearman Rank Correlation Coefficient (ρ) of Maize Grains and Soil obtained from Mining Sites

Metals	Maize (x)	Soil (y)	Rank (x)	Rank (y)	D	D^2
Pb	0.020	2.562	5	2	3	9
Ni	0.048	0.298	4	5	-1	1
Zn	0.260	1.522	1	3	-2	4
Cr	0.002	0.273	7	6	1	1
Cd	0.010	0.220	6	7	-1	1
As	0.093	2.876	3	1	2	4
Ag	0.104	0.532	2	4	-2	4
Total						24

$\rho \approx 0.93$

Table 8: Spearman Rank Correlation Coefficient (ρ) of Maize Grains obtained from Mining Sites and Control Sites

Metals	Maize(x)	Control(y)	Rank (x)	Rank (y)	D	D^2
Pb	0.020	0.013	5	4	1	1
Ni	0.048	0.013	4	4	0	0
Zn	0.260	0.014	1	3	-2	4
Cr	0.002	0.010	7	6	1	1
Cd	0.010	0.004	6	5	1	1
As	0.093	0.065	3	2	1	1
Hg	0.104	0.099	2	1	1	1
Total						9

$\rho \approx 0.84$

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

Table 7: Spearman Rank Correlation Coefficient (ρ) of maize grains and soil obtained from control site

Metals	Maize (x)	Soil (y)	Rank (x)	Rank (y)	D	D^2
Pb	0.013	1.722	4	1	3	9
Ni	0.013	0.127	4	6	-2	4
Zn	0.114	1.441	1	2	-1	1
Cr	0.010	0.138	5	5	0	0
Cd	0.014	0.180	3	3	0	0
As	0.065	0.148	2	4	-2	4
Hg	0.010	0.092	5	7	-2	4
Total						**22**

$\rho \approx 0.61$

4. Conclusion

Plants are known to take up and accumulate heavy metals from contaminated soil and sediments with variations in metal content dependent on several factors such as soil properties, plant species, plant age, and time interval of metallic soil input, nutrient availability and interaction among the metals. The concentration of Pb, Cd, As and Hg in maize grains grown in the mining site were found to be higher and slightly above the permissible limit, and most of the heavy metals are bioavailable for plants uptake even though the concentration of heavy metals are less than unity as indicated by the transfer factor.

Acknowledgement

We wish to appreciate Miss Mavis, Omovo, Mr Williams Daniel and Peter Ujulu of chemistry laboratory Federal University Wukari for their technical assistance towards the progress of this research work.

References

[1] United State Environmental Protection Agency (2002). *Supplemental guidance for developing soil screening levels for superfund sites*. Washington, D.C.

[2] Abdus-Salam, N., Ibrahim, M.S and Fatoyinbo, F.T. Dumpsites in Lokoja, Nigeria: A silent pollution zone for underground water. A *Journal of waste Management and Bioresource Technology*, 2011. 1(2): 21-30.

[3] Adekola, F.A., Abdus-Salam, N., Bale, R.B. and Oladeji, I.O. Sequential extraction of trace metals

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

and particle size distribution studies of Kainji lake sediment, Nigeria. *Chem. Spec. Bioavailab.* 2010, 22(1): 43- 49.

[4] Adriano, D. C. Trace elements in the terrestrial environment. *Springer*-Verlag New York 1986. 105-123, 533.

[5] Alloway, B. J. Heavy metals in soils, Blackie Academic & Professional, an imprint of Chapman & Hall, London. 1995. 11-37.

[6] Annan, K., Dickson, R.D., Amponsah, I.K. and Nooni, I.K. The heavy metals contents of some selected medicinal plants sample from different geographical locations. *Pharmacognosy Research.* 2013. 5(2):103-108.

[7] Chaney, R.L. *Metal speciation and interaction among elements affect trace element transfer in agricultural and environmental food-chains*. Lewis Publications, Boca Raton, Fla., 1988, pp. 219-259.

[8] Chen T. B., Wong, J. W. C., Zhou, H. Y., and Wong, M. H. Assessment of trace metal distribution and contamination in surface soils of Hong Kong. *J. Environmental Pollution* 1997. 96: 61-68

[9] Chen T.B., Zheng, Y.M., Lei, M. Huang, Z.C.and Chen, H. Assessment of heavy metal pollution in surface soils of urban parks in Beijing, *China Chemosphere*, 2005. 60: 542-551.

[10] Edebi, N.V., and Gideon, O. A. Evaluation of pharmacognostical parameters and heavy metals in some locally manufacture herbal drugs. *Journal of Chemistry and Pharmaceutical Research.* 2011. 3(2): 88-97.

[11] Fernandes, J. C. and Henriques, F. S. Biochemical, physiological and structural effects of excess copper in plants. *The Botanical Review,* 1991, 57: 246-273.

[12] Guala, S.D., and Vega, F.A. and Covelo, E.F. The dynamics of heavy metals in plant-soil interactions. *Ecological Modelling*. 2010, 221:1148-1152.

[13] Gupta, S. K., Vollmer, M. K. and Krebs, R. The importance of mobile, mobilisable and pseudo total heavy metal fractions in soil for three-level risk assessment and risk management. *Science of the Total Environment*. 1996, 178: 11-20.

[14] Hermelinda, P., Toru, I., Takeshi, K., Yoshihiro, O., and Mashashi Kamon. Speciation and Mobility Assessment of Zinc in Coastal Landfill Sites with MSW Incinerator Ash. *Journal of environmental engineering.* 2010, 136: 1-2.

[15] Itumoh, J., Izuagie, T.,Omaka,N. O., O., Uba, A., Shuaibu, M., Dogonyaro, I. A., Isah, A., Dange, A. U.and Isah, S. I. Trace metals analysis of soil and water samples from a lime stone mining Site in Sokoto state Nigeria. *Journal of Physical Sciences and Innovation. 2011,* 3(4): 43-50.

[16] Kaasalainen and M. Yli-Halla. Use of sequential extraction to assess metal partitioning in soils. *J.*

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

Environmental Pollution. 2003, 126(2): 225-233.

[17] Kabata-Pendias and H. Pendias. *Trace elements in soils and plants*, CRC Press, Boca Raton, Florida, USA, 3rd edition. 2001, Pp 67-70

[18] Kramer, J.R. and Allen, H.E., eds., *Metal Speciation: Theory, Analysis, and Application*, Lewis Publications, Boca Raton, Fla. 1988, p. 219-259.

[19] Li, F., Fan,Z., Xiao,P., Oh,K., Ma,X. and Hou,W. Contamination, chemical speciation and vertical distribution of heavy metals in soils of an old and large industrial zone in Northeast China. *Environmental Geology,* 2003, 57 (8): 1815-1824.

[20] Lokeshwari, H. Chandrappa, G.T. Impact of heavy metals contamination of Bellandur Lake on soil and cultivâtes végétation. *Current Science.* 2006, 91(5) : 622-627.

[21] Lu, A., Zhang, S and Shan, X-Q. Time effects on the fractionation of heavy metals in soils. *Geoderma*. 2005, 125: 225-234.

[22] Mapanda, F., Mangwayana, E. N., Nyamangara, J. and Giller, K. E. The effects of long-term irrigation using water on heavy metal contents of soils under vegetables. *Agriculture, Ecosystem Environment.* 2005, 107: 151-156.

[23] Martin S.E. and Griswold W. *Human health effects of heavy metals*. Center for Hazardous Substance Research (CHSR), Kansas State University. 2009, 15:6.

[24] McLaren, R. G., Clucas, L. M., Taylor, M. D. and Hendry, T. Leaching of macronutrients and metals from undisturbed soils treated with metal-spiked sewage sludge 1. Leaching of macronutrients. *Australian Journal of Soil Research.* 2003, 41: 571-588.

[25] McLaughlin, M. J. and Smolders, E. Background zinc concentrations in soil affect the zinc sensitivity of soil microbial processes–a rationale for a metallo region approach to risk assessment. *Environmental Toxicology and Chemistry.* 2001, 20: 2639-2643.

[26] Monika, Z. and Romic, M. *Soil contamination by trace metals. Geochemical behavior as an element of Risk assessment*, earth and environmental sciences, 2011, chapter 19, pp 438-446

[27]Narwal, R. P., Singh, B. R. and Salbu, B. Association of cadmium, zinc, copper and nickel with components in naturally heavy metal rich soils studied by parallel and sequential extraction. *Communications in Soil Science and Plant Analysis.* 1999, 30: 1209-1230.

[28] Oluwatson, G.A., Adeyolanu,O.D., Dauda,T.O. and G.E. Akinbola,G.E. Levels and geochemical fractions of Cd, Pb and Zn in valley bottom soils of some urban cities in South-Western Nigeria. *African Journal of Biotechnology. 2008,* **7** (19): 3455–3465.

[29] Opaluwa, O. D., Aremu, M. O., Ogbo, L. O., Abiola, K. A., Odiba, I. E., Abubakar, M.M. and Nweze,N.O. Heavy metal concentrations in soils, plant leaves and crops grown around dump sites

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

in Lafia Metropolis, Nasarawa State, Nigeria. *Journal of Advances in Applied Science Research.* 2012, **3** (2):780-784.

[30] Paquin, P. and Gorsuch, J.W., Apte, S., Batley, G.E. The biotic ligand model: a historical overview. *Comp Biochem Phys. 2002,* 133, 3-35.

[31] Ramirez, M., Massola, S., Frache, R. and Correa, J. Metal speciation and environmental impact on sandy beaches due to Elsavador copper mines, Chile, marine pollution. *Bulletin*. 2005, 50(1): 62-72.

[32] Remon, E., Bouchardon, J. L., Cornier, B., Guy, B., Leclerc, J. C. and Faure, O. Soil characteristics, heavy metal availability and vegetation recovery at a former metallurgical landfill: Implications in risk assessment and site restoration. *Environmental Pollution*. 2005, 137: 316-323.

[33] Ross, S. M. *Toxic metals in soil-plant system*, John Wiley & Sons, Chichester, West Sussex, England. 1994. p 481

[34] Sharma, R. K., Agrawal, M. and Marshall, F. Heavy metal contamination of soil and vegetables in suburban areas of Varanasi, India. *Ecotoxicology and Environmental Safety*. 2007, 66: 258-266.

[35] Sharma, R.K and Agwala, M. Biological effects of heavy metals: an overview. *Journal of Environmental Biology.* 2005, 26(2):301-13.

[36] Speir, T. W., Van-Schaik, A. P., Percival, H. J., Close, M. E. and Pang, L. P. Heavy metals in soil, plants and groundwater following high-rate sewage sludge application to land. *Water, Air and Soil Pollution.* 2003, 150: 319-358.

[37] Tack, F. M. G. and Verloo, M. G. Chemical speciation and fractionation in soil and sediment heavy metal analysis: a review. *International Journal of Environmental Analytical Chemistry*. 1995, 59: 225-238.

[38] Tamunobereton-ari I., Omubo-Pepple, V.B and Tamunobereton-ari N.A. Speciation of heavy metals (Cu, Pb, Ni) pollutants and the vulnerability of groundwater resource in Okrika of Rivers State, Nigeria. *American Journal of Scientific and Industrial Research.* 2010, 2(1): 69-77.

[39] Tessier, A., Campbell, P.G.C. and Blsson, M. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry.* 1979, 52(1): 45-53.

[40] Tiller, K. G. Urban soil contamination in Australia. *Australian Journal of Soil Research.* 1992, 30: 937-957.

[41] Tokalioglu, S., Karlal, S. and Birol, G. Application of a three-stage sequential extraction procedure for the determination of extractable metal contents in highway soil. *Turk. J. Chem.* 2003, 27: 333-346.

[42] United State Environmental Protection Agency.www.epa.gov/waterscience. 2006 edition p. 14

[43] Uwah, E.I., Ndahi, N.P. and Ogugbuaja,V.O. Study of the levels of some agricultural pollutants in

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

soils and waterleaf (talinum triangulare) obtained in Maiduguri, Nigeria. *Journal of applied sciences in environmental sanitation.* 2009, 4(2): 71-78.

[44] Wang, C. X., Mo, Z., Wang, H., Wang, Z. J. and Cao, Z. H.; The transport, time-dependent distribution of heavy metals in paddy crops. *Chemosphere.* 2003, 50: 717-723.

[45] World Health Organization Regional Office for Europe. *Air Quality Guidelines*, chapter 6.1.Arsenic, Copenhagen Denmark, 2ndedition, 2000. p.23.
http://www.euro.who.int/document/aiq/6_1_arsenic.pdf.

[46] World Health Organization, WHO. *Guidelines for irrigation water*. 5th edition. 2011.p 3

[47] Yoon, J., Cao, X., Zhou, Q. and Ma, L.Q. Accumulation of Pb, Cu and Zn in native plants growing on a contaminated Florida site. *Science of the total environment.* 2006, 368:456-464.

[48] Young, M and Crawford, J. W. Interactions and self-organization in the soil-microbe complex. *Science.* 2004, 304: 1634-1637.

[49] Yusuf, K.A. Sequential extraction of lead, copper, cadmium and zinc in soils near Ojota waste site. *Journal of Agronomy.* 2007, 6(2): 331-337.

[50] Zarcinas, B. A., Ishak, C. F., McLaughlin, M. J., Cozens, G. Heavy metals in soils and crops in Southeast Asia. 1. Peninsular Malaysia. *Environmental Geochemistry and Health.* 2004, 26: 343-357.

[51] Soon, Y. K. and Bates, T. E. Chemical pools of cadmium, nickel, and zinc in polluted soils and some preliminary indications of their availability to plants. *Journal of Soil Science*. 1982, 33: 477-488.

[52] Ahumada, I., Escudero, P., Adriana, C. M., Castillo, G., Ascra, L. and Fuentes, E. Use of sequential extraction to assess the influence of sewage sludge amendment on metal mobility in Chilean soils. *Journal of Environmental Monitoring.* 2004, 6: 327-334.

[53] Albores, A. F., Perez-cid, B., Gomes, E. F. and Lopez, E. F. Comparison between sequential extraction procedures and single extraction procedures and for metal partitioning in sewage sludge samples. *Analyst.* 2000, 125:1353-1357.

[54] Khairiah, J., Ding-Woei, Y., Habibah, J., Ahmad-Mahir, A., Aminah, A. and Ismail, B. S. Concentration of heavy metals in guava plant parts and soil in the Sungai Wangi Plantation, Perak, Malaysia. *International Journal of Agricultural Research.* 2009, 4: 310-316.

[55] Ure, A. M. and Davidson, C. M. *Chemical Speciation in the Environment*. Blackwell, Oxford. 2002. Chapter 10. P. 45

[56] Rauret, G. Extraction procedures for the determination of heavy metals in contaminated soil and sediment. *Talanta*. 1998, 46: 449-455.

[57] United Nations Environmental Protection Programme (UNEP), Nairobi. *Sustainable consumption*

Copyright © 2018 by Modern Scientific Press Company, Florida, USA

and production activities in Africa: Regional status report, 2002-2004. Nairobi Kenya. Page 25

[58] Amusan, A.A., Ige, D.V.and Olawale, R. Characteristics of Soil and Crop uptake of metals in municipal waste dumpsites in Nigeria. *J. Hum. Ecol. Kamla Rja.* 2005. 1 (2): 167-171

Copyright © 2018 by Modern Scientific Press Company, Florida, USA