Journal of Soil Science and Environmental Management Vol. 3(11), pp. 262-274, November 2012
Available online at http://www.academicjournals.org/JSSEM
DOI: 10.5897/JSSEM11.116

Full Length Research Paper

Assessment of metal contamination in soil and plants from abandoned secondary and primary goldmines in Osun State, Nigeria

Ekwue Y. A.[1]*, Gbadebo A. M.[1], Arowolo T. A.[1] and Adesodun J. K.[2]

[1]Department of Environmental Management and Toxicology, University of Agriculture, Abeokuta, Ogun State, Nigeria.
[2]Department of Soil Science and Land Management, University of Agriculture, Abeokuta, Ogun State, Nigeria.

Accepted 27 December, 2011

Heavy metal contamination of soil, water, and crops, and their health impact on residents, is a persistent social issue, and several studies have identified health risks of residents living near abandoned mines. In this study, the heavy metal concentrations in the soil and plants of abandoned gold mines of the primary goldmine and the secondary goldmine, Ilesa-Osun State Nigeria of latitude 7°, 27'N to 7°,35'N and longitude 4°, 47'E to 4°,53'E was investigated. A total of 20 soil samples in replicates of two [both surface (0 to15 cm) and subsurface (15 to 30 cm)] were collected from both sites and eight plant samples were also collected from both sites for this study. Metal concentration was determined using the Inductively Coupled Plasma/ Optical Emission Spectrometry (ICP/OES) technique. The trend of metal concentration was, Cr >Zn >Cu >Co >Pb >As >Cd. Soils in the secondary goldmine had mean values for Cu, Cr and Co higher than NCI standards for soil, which is indicative of Cu, Cr Co contamination in general. Chromium concentration of 79.4 mg/kg was observed in the soils of the secondary goldmine indicating chromium toxicity, at both 0 to 15 cm and 15 to 30 cm depths. While in plants, metal concentration was Zn >Cu >Pb> Cr >Co >As >Cd >Cd. Cd. Cu and Zn contamination in plants from the primary goldmine, were above the normal concentration of metals found in plants, with Cu considered to be at a high level, also (21 mg/kg). The plants considered in this study were observed to have high potential for phytoextraction of certain heavy metals.

Key words: Heavy metals, goldmines, contamination, soil, plants

INTRODUCTION

Mining gives rise to soil erosion and environmental contamination by generating waste during the extraction, beneficiation, and processing of minerals. After closure, mines can still impact the environment by contaminating air, water, soil, and wetland sediments from the scattered tailings, as well as pollution of groundwater by discharged leachate, unless the proper remediation is conducted. Heavy metal contamination of agricultural soils and crops surrounding the mining areas is a serious environmental problem in many countries, Nigeria inclusive (Aslibekian and Moles, 2003).

Recently, pollution of general environment has increasingly gathered a global interest. In this respect, contamination of agricultural soils with heavy metals has always been considered a critical challenge in scientific community (Faruk et al., 2006). Heavy metals are generally present in agricultural soils at low levels. Due to their cumulative behaviour and toxicity, however, they have a potential hazardous effect not only on crop plants but also on human health (Das et al., 1997). Heavy metal contamination of soil, water, and crops, and their health impact on residents, is a persistent social issue, and several studies have identified health risks of residents living near abandoned mines (Park et al., 1998; Chung et al., 2005).

Other researchers reported that concentrations of heavy metals, including Cd and Zn, in the soils are usually above the background levels, and generally

*Corresponding author. E-mail: yvonne_kw@yahoo.co.uk.

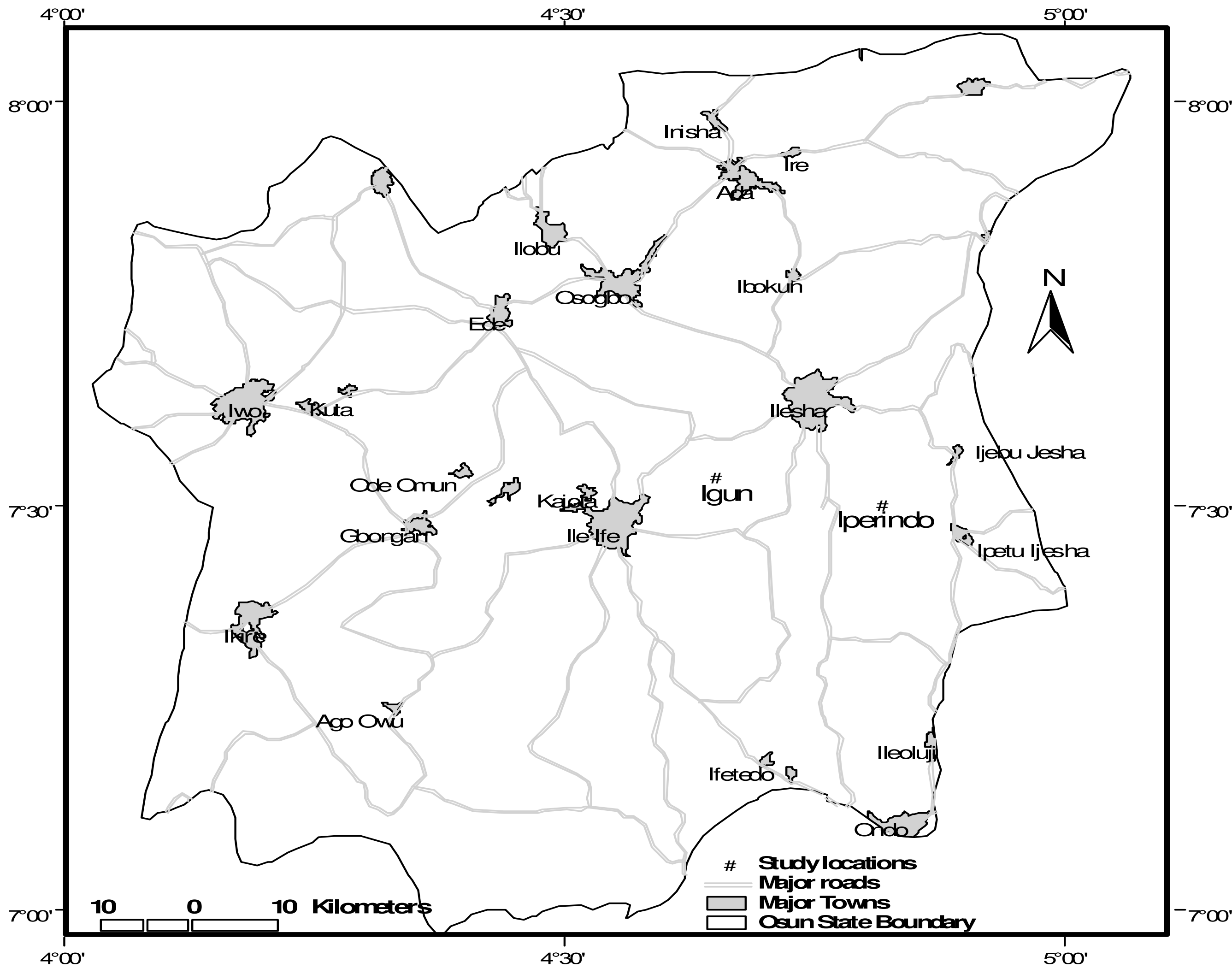

Figure 1. Map of Osun State showing study locations.

exceed the government guidelines for metals in soil (Wang et al., 2003). As well, the concentrations of metals in plants often serve to indicate the metal contamination status of the site, and also reveal the abilities of various plant species to take up and accumulate the metals from the soil.

In this study, the heavy metal concentrations in the soil and plants of abandoned gold mines of the primary goldmine and the secondary goldmine, Ilesa-Osun state Nigeria, was investigated.

MATERIALS AND METHODS

Description of study area

The primary goldmine - Odo Ilesa gold field - is located some 18 km south of Ilesa linked by asphalt road having compass direction of latitude 7°, 27'N to 7°,35'N and longitude 4°, 47'E to 4°,53'E (Figure 1). The old primary gold mine is in the Ilesa schist belt of southwestern Nigeria (Wikipedia, 2007).

The primary goldmine mineralization comprises a series of auriferous quartz-carbonate veins localized by a subsidiary fault within biotite gneiss and mica schist, presently defined by sub-parallel old working extending overall for about 900 m in a NNE direction. Gold occurs with pyrite, pyrrhotite and minor chalcopyrite, galena, sphalerite, magnetite and ilmenite (TML, 1996).

Similarly, the secondary goldmine which falls within the latitude 7, 53'N and longitude 4 ^{o}, 65'E, area is underlain predominantly by foliated amphibolites, migmatites, gneisses and schists (Wikipedia, 2008). Proven reserves of 68,768 ounces of gold hosted by 14,104,702 m^3 of ore at an average of 0.00488 oz/m^3 (NMC, 1987). Four broad groups of well-drained soil types namely Okemesi, Ondo, Egbeda and Itagunmodi soil types, characterized the study area (TML, 1996). The Okemesi soil type, derived from unweathered quartzite ridge beneath the stable segment, is characterized by very coarse greyish brown to brownish grey sand fraction. The sandy Ondo and the clayey Itagunmodi soil types derived from variably migmatised gneiss, biotite-and biotite-hornblende-gneiss and weathered amphibolites respectively. The area is drained by rivers Oni and Owena which flow in an approximately N-S direction. The drainage pattern is dendritic. The tributary streams take their courses from the surrounding hills (Wikipedia, 2008).

Field work

This aspect of the study comprised of soil, and plants sampling and preservation. A GPS was used to take coordinates during sample collection.

Soil sampling/treatment

A total of 20 soil samples in replicates of two [both surface (0 to15 cm) and subsurface (15 to 30 cm)] were collected from both sites. The soil samples from the primary goldmine were collected randomly, starting 50 m away from the open cast while subsequent ones were collected at an interval of 200 m, using a soil auger. However, at the secondary goldmine, soil samples were randomly taken at an interval of 250 m to cover the area around the mining site.

The soil samples collected were air-dried, the soil was ground using a mortar and pestle and sieved through a 2 mm mesh to remove, stones and other plant materials (Rana et al., 2010) these were then packaged for necessary laboratory analysis both in the Department of Environmental Management and Toxicology, Laboratory UNAAB - Alabata and Activation Laboratory Ontario, Canada.

Plant sampling and preservation

Plant samples were collected from exactly the same point as soil samples; for small plants, the whole plant was taken but for large ones, only the shoot was taken. Only plant species found frequently in the two study areas were analyzed. At the end of the sampling only two major plants were found to be common to both the secondary goldmine and the primary goldmine, the plants were identified to be ferns (*Selanginella* spp.), in all, 8 plant samples were generated (that is, each of the two was separated into above ground biomass and root).

Then, samples were washed with tap water, quickly rinsed with 0.1 mol L^{-1} HCl and severally rinsed with deionized water. Samples were then dried at 70°C for 3 days; this was done in accordance with the method of Ma et al. (2001); all plant materials were ground in a mill prior to further analysis and metal determination.

Determination of physicochemical properties of the soil

The pH was determined by the method of Carter and Gregorich (1994), Particle size analysis by (hydrometer method), CEC by ammonium acetate method Thomas (1982), available phosphorus by Bray 1 method, organic matter content by the method of Nelson and Sommers (1982).

Determination of metals

Analysis of metals was carried out for the plants, rock and tailing samples. Prior to this, 0.5 g of each sample was digested with 0.5 ml H_2SO_4, 0.6 ml concentrated HNO_3 and 1.8 ml concentrated HCl for 2 h at 95°C. Samples were cooled then diluted to 10 ml with deionized water; these were then analyzed using Inductively Coupled Plasma/ Optical Emission Spectrometry ICP/OES technique on a Varian Vista 735 ICP for the 35 element suite, in optimum condition. A matrix standard and blank was run every 13 samples. A series of USGS and OREAS geochemical standards were used as controls (ACTLABS, 2008). The detection limits for metals were 1 ppm for Cr, Co, Cu, 2 ppm for Pb, As, and Zn, 0.01% for Fe, Ca, K, Mg and 0.001% for Na.

Data analysis

Data generated from both field and laboratory were subjected to both basic descriptive and detailed statistics of standard deviation correlation and LSD; which were achieved using: Microsoft excel for data entry, SAS for mean, range, ANOVAs and mean separation (LSD). The data for the soil samples were subjected to principal component analysis and correlation analysis using, SYSTAT version 8.0 software. Principal component analysis (PCA) was performed using the metal dry weight concentration data. As PCA requires a complete matrix with no missing data, a random number generation process was used to replace non-detects with levels between 0.01 and 0.5, the detection limit of each element. The correlation and principal component analysis were used in this study, in order to have a multivariate view and a good representation of the overall level of metal interaction as well as to reflect the possible source of the metals found in the soils of the study area.

RESULTS

Soil sample analysis

Soils ranged between clay loam to loam sand in the secondary goldmine, while at the primary goldmine, the soils were loam sand to sand, majority being sand (Table 1). The pH values of the soil samples in the secondary goldmine (Table 1) ranged from 4.7 to 7.6 with a mean value of 5.8. In the primary goldmine, the pH ranged was 4.4 to 6.5 with a mean value of 5.54 (Table 1). EC ranged from 47 to 590 µS/Cm with a mean value of 298.2 µS/Cm in the primary goldmine and 24 to 244 µS/Cm with a mean value of 72.4 µS/Cm in the secondary goldmine. Furthermore, available phosphorus ranged from 0.94 to 12.52 with a mean value of 4.79 mg/L in the secondary goldmine, while in the primary goldmine, it ranged from 0.035 to 11.3 mg/L with a mean value of 6.55 mg/L, CEC ranged from 5.56 to 30.75 meq/100 g with a mean value of 16.89 meq/100 g in the secondary goldmine and in the primary goldmine, the range was from 7.76 to 11.37 meq/100 g with a mean value of 19.29 meq/100 g (Table 1). The percentage organic carbon (%OC) ranged from 0.08 to 4.19, with a mean value of 2.93 and from 2.78 to 18.69 with a mean value of 4.47 in the secondary goldmine and the primary goldmine respectively (Table 1). Also, percentage organic matter (%OM) ranged from 1.38 to 7.22, with a mean value of 5.09 in the secondary goldmine and ranged from 4.79 to 32.22 with a mean value of 7.704 for the primary goldmine (Table 1).

Results for soil sample metal analysis (Table 2) also showed that in the secondary goldmine, metal concentrations generally ranged from <0.5 to 0.7 mg/kg for Cd, 8 to 15 mg/kg for Pb, 62 to 131 mg/kg for Cr, <2 to 2 mg/kg for As, 1 to 47 mg/kg for Co, 9 to 49 mg/kg for Zn and 10 to 42 mg/kg for Cu, the mean values at 0 to 15

Table 1. Physicochemical characteristics of soil samples from both the primary and secondary goldmines.

Sample	pH in water	EC (µS/cm)	CEC (Meq/100 g soil)	Available phosphorus (Mg/L)	Organic carbon (%)	Organic matter (%)	Sand (%)	Clay (%)	Silt (%)	Texture
Secondary goldmine										
1	5.5	47	30.75	12.52	4.19	7.22	80.8	10.8	8.4	Sand
2	4.7	35	5.56	8.83	3.39	5.85	73.6	24	22.4	Loam sand
3	7.6	244	29.01	0.939	1.79	3.09	73.6	9.6	16.8	Loamy sand
4	5.7	24	7.30	8.972	0.08	1.38	44.8	29.7	25.5	Clay loam
5	5.5	112	11.88	5.286	3.99	5.85	4.6	37.8	16.2	Clay loam
Mean	5.8	92.4	16.9	7.3094	2.688	4.678	-	-	-	-
SD	1.077	91.379	12.087	4.384	1.735	2.377	-	-	-	-
Range	4.7-7.6	35-244	5.56-30.75	0.94-12.52	0.08-4.19	1.38-7.22	-	-	-	-
Primary goldmine										
1	6.5	47	11.46	0.035	18.69	32.22	97.3	1.35	1.35	Sand
2	4.4	475	24.46	0.001	2.78	4.79	89.2	0	10.8	Sand
3	6.3	60	11.37	0.035	4.19	7.22	88	5.4	6.6	Sand
4	4.8	590	20.49	0.069	4.59	7.91	86.5	5.4	8.1	Sand
5	5.7	319	28.69	11.3	5.99	10.32	78.4	8.1	13.5	Loam sand
Mean	5.54	298.2	19.294	2.288	7.248	12.492	-	-	-	-
SD	0.92	243.25	7.76	5.04	6.49	11.20	-	-	-	-
Range	4.4-6.5	47-590	11.37-28.69	0.001-11.30	4.19-18.69	4.79-32.22	-	-	-	-

1 to 5 represent samples from each point.

Table 2. Metal concentrations of soil samples at 0 to 15 cm depth from both the secondary and primary goldmines.

Sample	Cd (mg/kg)	Pb (mg/kg)	Cr (mg/kg)	As (mg/kg)	Co (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Sum of metals	Fe (%)	Na (%)	Ca %)	K (%)	Mg (%)
Secondary goldmine													
S1	0.7	11	117	< 2	18	45	36	229.67	6.77	0.03	0.16	0.13	0.24
S2	0.6	8	67	< 2	9	34	26	146.55	4.87	0.02	0.02	0.03	0.03
S3	< 0.5	15	62	< 2	45	49	40	213.45	4.54	0.03	0.38	0.06	0.1
S4	0.6	11	86	< 2	13	38	36	186.54	6.19	0.02	0.03	0.03	0.05
S5	< 0.5	10	65	< 2	42	49	27	195.45	4.52	0.04	0.02	0.07	0.09
Mean ± SD	0.56 ± 0.11	11.00 ± 2.55	79.40 ± 23.02	1.83 ± 0.11	25.40 ± 16.86	43.00 ± 6.75	33.00 ± 6.16	-	5.38 ± 1.04	5.38 ± 1.04	0.12 ± 0.16	0.05 ± 0.05	0.10±0.08
Range	0.42-0.7	8-15	62-117	1.72-2	9-42	34-49	27-40	-	4.52-6.77	0.02-0.04	0.02-0.38	0.03-0.07	0.03-0.24
Primary goldmine													

Table 2. Contd.

S1	< 0.5	6	5	< 2	1	9	10	33.45	0.95	0.02	0.03	0.07	0.05
S2	< 0.5	15	27	< 2	5	26	8	83.45	1.98	0.02	0.22	0.16	0.17
S3	< 0.5	14	19	< 2	8	15	5	63.45	1.15	0.02	0.1	0.07	0.06
S4	< 0.5	32	21	< 2	9	23	11	98.43	1.44	0.03	0.14	0.1	0.11
S5	< 0.5	9	19	21	4	24	17	94.47	1.13	0.03	0.19	0.16	0.16
Mean ± SD	0.42 ± 0.07	15.20 ± 9.62	18.2 ± 16.66	1.80 ± 0.64	5.40 ± 2.82	19.40 ± 6.65	10.20 ± 4.26	-	1.48 ± 0.52	0.02 ± 0.00	0.17 ± 0.11	0.12 ± 0.04	0.13 ± 0.06
Range	0.41-0.5	6-32	5-27	1.61-21	1-9	9-26	5-13	-	0.95-6.78	0.02-0.03	0.03-0.22	0.07-0.16	0.05-0.17
CRM (mg/kg))	1	101	96	330	13.8	118	66	-	-	-	-	-	-
NCI (mg/kg)	0.1-1.0	1-20	2-50	-	1-10	3-50	1-20	-	-	-	-	-	-
MAL (mg/kg)	3	100	50	-	-	300	100	-	-	-	-	-	-

CRM, Certified reference material (Actlabsint, 2009); SD, standard deviation; NCI, normal content intervals of heavy metals in soils (Kloke, 1980); MAL, maximum allowable limits for heavy metals in soil (mg/kg) (Kabata-Pendias, 1995).

cm depths were 0.56 mg/kg Cd, 33 mg/kg Cu, 11.0 mg/kg Pb, 43 mg/kg Zn, 1.83 mg/kg As, 79.40 mg/kg Cr, 25.4 mg/kg Co; for the 15 to 30 cm depth mean values are 0.57 mg/kg Cd, 30.8 mg/kg Cu, 10.4 mg/kg Pb, 35.2 mg/kg Zn, 1.86 mg/kg As, 72.8 mg/kg Cr and 18 mg/kg Co. In the primary goldmine (Table 2), Cd value was generally <0.5, Cu ranged from 5 to 19 mg/kg, Pb ranged from 6 to 33 mg/kg, Zn from 9 to 31 mg/kg, As from <2 to 21 mg/kg, Cr from 5 to 27 mg/kg, Co 1 to 9 mg/kg, themean values for metals at 0 to 15 cm depth are 0.42 mg/kg Cd, 10.2 mg/kg Cu, 15.2 mg/kg Pb, 19.4 mg/kg Zn, 1.82 mg/kg As, 18.2 mg/kg Cr, 5.4 mg/kg Co; similarly, at 15 to 30 cm, the mean values are 0.44 mg/kg for Cd, 12 mg/kg for Cu, 16.2 mg/kg for Pb, 21.6 mg/kg for Zn, 1.76 mg/kg for As, 20.4 mg/kg for Cr, 6.2 mg/kg for Co (Figure 2).

Correlation analysis between metal concentrations at 0 to 15 cm and 15 to 30 cm depth in the secondary goldmine (Table 3) revealed a highly significant relationship ($p \leq 0.01\%$) between cadmium in 0 to 15 cm level and cadmium concentration in the 15 to 30 cm level, with a highly significant but negative relationship between arsenic in 0 to 15 cm depth and cobalt in 15 to 30 cm depth. Furthermore in the primary goldmine, highly significant relationship was observed between cadmium at 0 to 15 cm depth and chromium at 15 to 30 cm depth, Pb at 0 to15 cm and 15 to 30 cm depths, same for Co. This kind of relationship existed between As and Zn at 0 to 15 cm depth (Table 4).

PCA results for the secondary goldmine (Table 5) revealed that at 0 to 15 cm and 15 to 30 cm depths each, three of the principal components had Eigen values greater than 1.0; these principal components (that is, for 0 to 15 cm depth in the secondary goldmine) recorded Eigen values of 3.866, 3.109 and 0.827 respectively, thereby, all accounting for 97.536% of the variation among soil samples.

The PC1 that accounted for 48.330% of the variability in all metals were of significant values except Cu (0.297). PC2 accounted for 38.865% of the total variation and the variation was related to all the metals except Co (0.005) and Zn (0.271). The PC3 accounted for 10.342% of the total variation and was dominated by Cr (0.433), As (0.369), and Zn (0.550). At the 15 to 30 cm depth, the recorded Eigen values of 4.569, 2.501 and 0.870 respectively, all accounting for 97.251% of the variation among soil samples. The PC1 accounted for 57.111% of the variability in all metals were of significant values in this component, PC2 accounted for 31.268% of the total variation and the variation was related to all the metals except Zn (0.200) and Cu (0.096). The PC3 accounted for 10.872% of the total variation and was dominated by Pb (0.348) and As (0.777).

PCA for the primary goldmine (Table 6) also revealed three components for 0 to 15 cm depth, accounting for 58.200, 19.723 and 17.307% of the total variance of the model. According to the PCA model, Cd, Cu and Fe were strongly loaded (component coefficient ≥ 0.30) onto a different component axis (PC2) than the other metals (PC1); at PC3, the exceptions were Cr (0.252), As (0.174) and Cu (0.290). The PCA for the 15 to 30 cm depth revealed three components jointly accounting for 94.252% of the total variation with 40904, 33.738 and 19.610% for PC1, PC2 and PC3 respectively. Most of the metals had significant contribution to variations present in the soil samples in the three components identified though

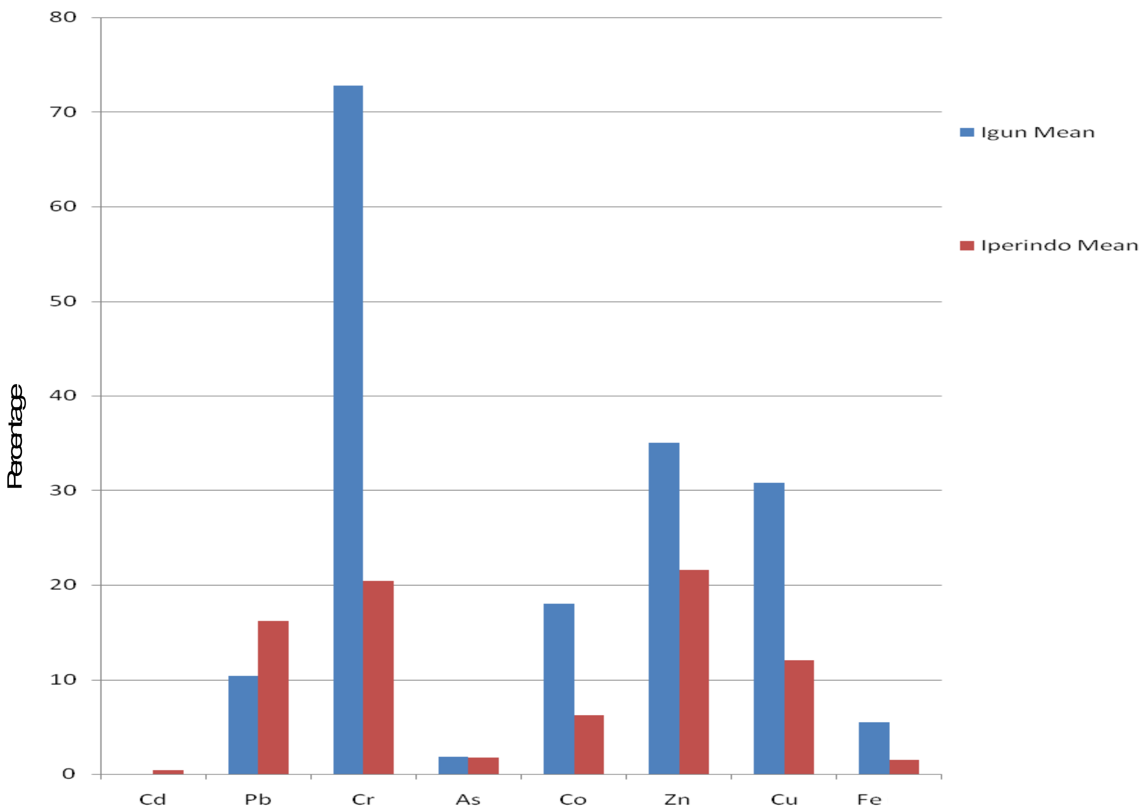

Figure 2. Average metal concentration in soil samples at 15 to 30 cm depth for the secondary and primary goldmines.

there were some exceptions, thus; Cd (0.078) and Co (0.135) at PC1,Zn (0.090) and Fe (0.264) for PC2, Cr(0.138) and As (0.104) of less contribution in PC3.

Plant sample analysis

The results for plant metal analysis (Table 7) revealed that the Cd concentration was generally <0.5 mg/kg, however, Pb ranged from <2 to 5 mg/kg, Cr ranged from 1 to 6 mg/kg, As was generally <2 mg/kg, Zn ranged from 26 to 53 mg/kg and Cu ranged from 4 to 26 mg/kg. The mean concentrations in the shoot was 0.465 mg/kg for Cd, 8.5 mg/kg for Cu, 1.90 mg/kg for Pb, 27.5 mg/kg for Zn, 1.855 mg/kg for As, 4.5 mg/kg for Cr, 3.0 mg/kg for Co, while it was 0.446 mg/kg for Cd, 5.0 mg/kg for Cu, 1.925 mg/kg for Pb, 27.5 mg/kg for Zn, 1.816 mg/kg for As, 1.5 mg/kg for Cr, 0.935 mg/kg for Co for the roots in the secondary goldmine location. While in the primary goldmine, mean values in shoots were 0.962 mg/kg for Cd, 21 mg/kg for Cu, 4.5 mg/kg for Pb, 47 mg/kg for Zn, 1.96 mg/kg for As, 2.5 mg/kg for Cr, and 0.945 mg/kg for Co, with 0.47 mg/kg for Cd, 18.5 mg/kg for Cu, 2.48 mg/kg for Pb, 40.5 mg/kg for Zn, 1.87 mg/kg for As, 3 mg/kg for Cr, and 2 mg/kg for Co in the roots of the plants.

The means of metal concentrations found in the roots of plants from the secondary goldmines, showed no significant difference to those of the plant roots from the primary goldmines at $p \leq 0.05$ level (Table 8). Whereas for the plant shoots, there were differences between the means of plant shoots from the secondary goldmines as compared to those from primary goldmines ($p \leq 0.05$) in this trend Cu>Pb>K>Ca>Co>Mg (Table 9) with Cu having the highest value of 8.87 at $p \leq 0.05$ level. The bioconcentration factor (BF) (Table 10) in the secondary goldmine for metals ranged from 0.057 to 1.014, As (1.014) having values >1, in the primary goldmine, the range was 0.137 to 2.423, with Cd (1.145), Cu (2.058), Zn (2.423), and As (1.069) having values >1. Similarly, the results for translocation factor (TF) shows (Table 11) that in the secondary goldmine, the range was 0.98 to 3.21, with Cd (1.04), Cu (1.70), Zn (1), Cr (3.00), Co (3.21) having values >1, while in the primary goldmine, TF ranged from 0.47 to 1.82, as Cd (1.06), Cu (1.14), Pb (1.82), Zn (1.16) and As (1.05) recorded values >1 (Table 11).

DISCUSSION

On comparing the data for soil samples from the

Table 3. Pearson's correlation matrix for 0 to 15 cm and 15 to 30 cm depths for soil samples at the secondary goldmine.

	Cd2	Pb2	Cr2	As2	Co2	Zn2	Cu2	Cd1	Pb1	Cr1	As1	Co1	Zn1	Cu1
Cd2	1	-0.016	0.882*	0.090	-0.183	0.360	0.370	0.987**	-0.369	0.865	-0.023	-0.825	-0.522	0.092
Pb2		1	0.442	-0.225	0.899*	0.885*	0.920*	0.135	0.788	-0.012	-0.878	0.102	0.055	0.869
Cr2			1	-0.100	0.282	0.743	0.742	0.936*	0.090	0.816	-0.469	-0.620	-0.337	0.528
As2				1	-0.609	-0.432	-0.157	0.042	-0.453	-0.035	0.640	-0.478	-0.556	-0.271
Co2					1	0.842	0.753	-0.041	0.882*	-0.097	-0.972**	0.401	0.363	0.810
Zn2						1	0.957*	0.495	0.618	0.328	-0.913*	-0.123	-0.029	0.817
Cu2							1	0.508	0.554	0.287	-0.806	-0.256	-0.204	0.807
Cd1								1	-0.266	0.830	-0.155	-0.816	-0.537	0.198
Pb1									1	-0.077	-0.850	0.646	0.654	0.875
Cr1										1	-0.137	-0.474	-0.060	0.324
As1											1	-0.291	-0.352	-0.868
Co1												1	0.906*	0.224
Zn1													1	0.361
Cu1														1

**Correlation is significant at the 0.01 level (2-tailed); * Correlation is significant at the 0.05 level (2-tailed); 1= 0 to 15 cm depth; 2 = 15 to 30 cm depth.

Table 4. Pearson's correlation matrix for 0 to 15 cm and 15 to 30 cm depths for soil samples at the primary goldmine.

	Cd2	Pb2	Cr2	As2	Co2	Zn2	Cu2	Cd1	Pb1	Cr1	As1	Co1	Zn1	Cu1
Cd2	1	0.156	-0.670	0.484	-0.475	-0.384	-0.048	-0.629	0.178	-0.324	-0.473	-0.256	-0.327	-0.350
Pb2		1	0.576	0.302	0.671	0.259	-0.058	0.661	0.978**	0.352	0.494	0.761	0.381	0.028
Cr2			1	0.062	0.717	0.687	0.269	0.983**	0.495	0.369	0.690	0.586	0.517	0.539
As2				1	-0.401	0.451	0.807	-0.025	0.144	-0.558	-0.264	-0.369	-0.192	0.560
Co2					1	0.044	-0.429	0.832	0.704	0.575	0.611	0.967**	0.386	-0.195
Zn2						1	0.685	0.559	0.156	0.209	0.587	-0.050	0.614	0.945*
Cu2							1	0.112	-0.247	-0.568	-0.183	-0.542	-0.138	0.864
Cd1								1	0.602	0.432	0.701	0.724	0.505	0.378
Pb1									1	0.494	0.554	0.823	0.455	-0.113
Cr1										1	0.900*	0.633	0.889*	-0.092
As1		;									1	0.607	0.962**	0.306
Co1												1	0.415	-0.323
Zn1													1	0.351
Cu1														1

**Correlation is significant at the 0.01 level (2-tailed); * correlation is significant at the 0.05 level (2-tailed); 1 = 0 to 15 cm depth; 2 = 15 to 30 cm depth.

Table 5. PCA of soil samples from the secondary goldmine at 0 to 15 cm and 15 to 30 cm depths.

Variable	0 to 15 cm			15 to 30 cm		
	PC1	**PC2**	**PC3**	**PC1**	**PC2**	**PC3**
Eigen value	3.866	3.109	0.827	4.569	2.501	0.870
Total variance (%)	48.330	38.865	10.342	57.111	31.268	10.872
Cummulative variance (%)	48.330	87.194	97.536	57.111	88.380	99.251
Cd	**-0.833**	**0.514**	-0.077	**0.520**	**0.808**	-0.255
Pb	**0.721**	**0.668**	-0.147	**0.827**	**-0.440**	**0.348**
Cr	**-0.615**	**0.655**	**0.433**	**0.857**	**0.495**	-0.142
As	**-0.399**	**-0.801**	**0.369**	**-0.306**	**0.550**	**0.777**
Co	**0.962**	-0.005	0.271	**0.724**	**-0.687**	-0.011
Zn	**0.784**	0.271	**0.550**	**0.978**	-0.200	-0.031
Cu	0.297	**0.915**	0.181	**0.962**	-0.096	0.242

Bolded value: Significant contribution; PCA = principal component analysis.

Table 6. PCA of metals in soil samples from the primary goldmine at 0 to 15 cm and 15 to 30 cm depths.

Variable	0 to 15 cm			15 to 30 cm		
	PC1	**PC2**	**PC3**	**PC1**	**PC2**	**PC3**
Eigen value	4.656	1.578	1.401	3.272	2.699	1.569
Total variance (%)	58.200	19.723	17.507	40.904	33.738	19.610
Cummulative variance (%)	58.200	77.924	95.431	40.904	74.642	94.242
Cd	**0.687**	**0.524**	**0.480**	-0.078	**-0.744**	**0.633**
Pb	**0.742**	0.127	**0.472**	**0.586**	**0.368**	**0.711**
Cr	**0.920**	0.212	0.252	**0.682**	**0.718**	-0.138
As	**0.956**	0.213	0.174	**0.713**	**-0.622**	0.104
Co	**0.774**	0.205	**0.587**	0.135	**0.924**	**0.330**
Zn	**0.895**	0.169	**0.412**	**0.885**	0.090	**-0.362**
Cu	0.079	**0.936**	0.290	**0.706**	**-0.434**	**-0.487**
Fe	**0.681**	**0.500**	**0.506**	**0.806**	-0.264	**0.341**

Bolded value: Significant contribution.

secondary goldmine and the primary goldmine, Pb and As were found to be higher in the primary goldmine while Cd, Cu, Zn, Cr and Co (0.56, 33.00, 43.00, 79.40, and 25.400 mg/kg) were higher in the secondary goldmine as against the values recorded in the primary goldmine (0.42, 10.20, 19.40, 18.20 and 5.40 mg/kg) for Cd, Cu, Zn, Cr and Co respectively. Similar trend was reported by Diatta et al. (2003) for mean values of these heavy metals in Poznan-Poland mining site. On comparing these values with the normal content intervals (NCI) in soils (Kloke, 1980), it was observed that Cu, Cr, and Co concentrations were above the normal content intervals in soils, while Zn and Pb were within the limits. This means that the soil of the secondary goldmine was contaminated with Cu, Cr and Co, though these concentrations are still within the maximum allowable limits (MAL) used in Poland (Kabata-Pendias, 1995), but the average chromium values was higher than the MAL used in Great Britain (Kabata-Pendias, 1995); this indicates that the level of chromium contamination in the secondary goldmine could be toxic to the growth of agricultural crops.

Furthermore, the results on depth basis show that the average concentration of Co, Cu, Pb, Cr and Zn in the secondary goldmine soils were higher at 0 to 15 cm depth, while Cd and As were found to have higher values at 15 to 30 cm depth. This conforms to the report of Nyangababo and Hamya (1985) which indicated that surface soils (0 to 15 cm) are better indicators of metallic burdens and the report of McBride et al. (1997) which showed that Cu is not readily leached from the soil profile and tends to accumulate in the surface soil due to its affinity for organic matter. Whereas in the primary goldmine all metal concentrations were within the normal content interval of Kloke (1980) considered for heavy metals in soil, only Cd and As showed higher mean values at the depth range of 0 to 15 cm. While Cd, Cu, Pb, Zn, Cr and Co were higher in 15 to 30 cm; this could be attributed to leaching effect as a result of long period of abandonment (over 15 years) of the mining site.

Table 7. Metal concentrations in plant samples from both the secondary and primary goldmines.

Sample	Cd (mg/kg)	Pb (mg/kg)	Cr (mg/kg)	As (mg/kg)	Co (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Na (%)	Ca (%)	K (%)	Mg (%)
Secondary goldmine											
P1A	<0.5	<2	1	<2	<1	28	4	0.27	0.06	0.52	1.42
P2A	<0.5	<2	2	<2	1	27	6	0.28	0.19	0.61	1.32
Mean±SD	0.44±0.02	1.90±0.06	1.50±2.16	1.81±0.02	0.93±1.19	27.50±1.29	5.00±2.21	0.08±0.03	0.56±0.10	1.37±0.17	0.27±0.01
P1B	<0.5	2	6	<2	3	29	9	0.25	0.76	0.36	1.64
P2B	<0.5	<2	3	<2	3	26	8	0.26	0.65	0.43	1.68
Mean±SD	0.46±0.02	1.92±0.06	4.50±1.31	1.86±0.03	3±1.19	27.5±1.29	8.50±2.22	0.06±0.03	0.39±0.11	1.66±0.17	0.26±0.01
Primary goldmine											
P3A	<0.5	<2	3	<2	3	28	11	0.3	0.56	0.61	1.69
P4A	<0.5	3	3	<2	1	53	26	0.39	0.25	1.08	1.56
Mean±SD	0.45±0-03	2.47±1.31	3.00±0.5	1.86±0.07	2.00±1.00	40.50±11.9	18.50±6.5	0.08±0.01	0.85±0.20	1.63±0.22	0.35±0.03
P3B	<0.5	4	2	<2	1	41	19	0.33	0.25	0.67	1.35
P4B	<0.5	5	3	<2	<1	53	23	0.36	0.13	0.8	1.17
Mean±SD	0.48±0.03	4.50±1.31	2.50±0.50	1.96±0.07	0.95±1.01	47±11.93	21±6.50	0.06±0.01	0.74±0.21	1.26±0.23	0.34±0.04
Range	0.01-0.49	0.56-5	1-6	0.02 - 1.97	26-53	4-26	4-26	0.25-0.39	0.06-0.65	0.36-1.08	1.17-1.69
CRM	1	101	96	330	13.80	118	66	-	-	-	-
NMC (mg/kg)	0.1-2.4	5-10	0.03-14	0.02-5	-	1-40	5-20	-	-	-	-
TMC (mg/kg)	5-30	30-100	5-30	5-20	-	100-400	20-100	-	-	-	-

A = Plant root; B = Plant shoot; NMC, normal metal concentration generally found in plants (Alloway and Ayres, 1993); TMC, phytotoxic metal concentration generally found in plant leaves (Alloway and Ayres, 1993).

Ahumada et al. (2007) reported similar concentrations for 0 to 10 cm and 10 to 30 cm for arsenic with the 0 to 10 cm having the highest concentrations. Also, Baker (1990) reported that higher copper concentration in surface layer of a soil is an indication of soil additions, from smelters, fertilizers, sewage sludges, and other wastes, pesticides and manures while Audu and Lawal (2005) noted that high concentrations of the metals could be attributed to the untreated tannery effluents, run-off of fertilizers from the farmlands, wastes dumped into the river, their availability in the earth crust, etc. Therefore, it could be concluded that the contamination of the soil with Cd, Cu, Pb, As and Cr recorded in this study is probably of geogenic and with some anthropogenic influence, which include mainly the use of agricultural inputs. Contaminated soils pose a risk to agricultural production, as the contaminants could easily be absorbed by plants.

It is important to note that plants posses highly specialized mechanisms to stimulate metal bioavailability in the rhizosphere and to enhance uptake into roots (Romheld and Marschner, 1986). Thus, the plants (*Selanginella* sp.) studied were analyzed to determine their metal contents and the result based on basic statistical analysis, showed that generally Zn >Cu >Pb >Cr >Co >As >Cd average values ranged from 0.47 to 27.5 mg/kg in shoots and 0.45 to 27.5 mg/kg in roots

Table 8. LSD among metals, in plant roots from the secondary and primary goldmines.

Parameter	Secondary goldmine	Primary goldmine	LSD (0.05)
Na	0.09	0.08	NS
Ca	0.57	0.85	NS
K	1.37	1.63	NS
Mg	0.28	0.35	NS
Cd	0.45	0.45	NS
Pb	1.90	2.48	NS
Cr	1.50	3.00	NS
As	1.82	1.87	NS
Co	0.94	2.00	NS
Zn	27.50	40.50	NS
Cu	5.00	18.50	NS
Fe	0.13	0.41	NS

NS = not significant at p≤0.05.

Table 9. LSD among metals, in plant shoots from the secondary and primary goldmines.

Parameter	Secondary goldmine	Primary goldmine	LSD (0.05)
Na	0.06	0.06	NS
Ca	0.39	0.76	0.32
K	1.66	1.26	0.39
Mg	0.26	0.35	0.07
Cd	0.47	0.49	NS
Pb	1.93	4.50	2.18
Cr	4.50	2.50	NS
As	1.86	1.96	NS
Co	3.00	0.95	0.24
Zn	27.50	47.00	NS
Cu	8.50	21.00	8.87

NS = Not significant at p≤0.05.

Table 10. Bioconcentration factors for plant samples from the secondary goldmine and the primary goldmine.

Metal	Mean concentration in shoots (mg/kg)	Bioconcentration factor	Remark
Secondary goldmine			
Cd	0.47	0.83	<1
Cu	8.50	0.26	„
Pb	1.93	0.18	„
Zn	27.50	0.64	„
As	1.86	1.01	>1
Cr	4.50	0.06	„
Co	3.00	0.12	„
Primary goldmine			
Cd	0.48	1.15	>1
Cu	21.0	2.06	„
Pb	4.50	0.29	<1
Zn	47.0	2.42	>1

Table 10. Contd.

As	1.96	1.07	>1
Cr	2.50	0.14	<1
Co	0.95	0.18	„

Values >1 Indicate usefulness of plant for phytoaccumulation (that is, root capable of accumulating metals) (Brooks, 1998).

Table 11. Translocation factor (TF) for plant samples from the secondary and primary goldmines.

Metal	Primary goldmine mean values (mg/kg)				Secondary goldmine mean values (mg/kg)			
	Shoot	Root	TF	Remarks	Shoot	Root	TF	Remarks
Cd	0.48	0.45	1.06	>1	0.47	0.45	1.04	>1
Cu	21.00	18.50	1.14	>1	8.50	5.00	1.70	>1
Pb	4.50	2.475	1.82	>1	1.90	1.93	0.98	<1
Zn	47.00	40.50	1.16	>1	27.50	27.50	1.00	1
As	1.96	1.87	1.05	>1	1.86	1.82	1.02	>1
Cr	2.50	3.00	0.83	<1	4.50	1.50	3.00	>1
Co	0.95	2.00	0.473	<1	3.00	0.94	3.21	>1

Values >1 Indicate usefulness of plant for phytoextraction (that is, shoot capable of accumulating metals) (Brooks, 1998).

for the secondary goldmine, while in the primary goldmine, 0.95 to 47 mg/Kg in shoots and 0.47 to 40.5 mg/Kg in roots. Porebska and Ostrowska (1999) reported that the content of elements in the biomass depends mainly on the amount of mineral constituents present in the soil in the form that is available to plants as well as the type of the species and the development phase of the plant. The result revealed that, cadmium levels was higher in the shoot with an average value of 0.465 mg/kg in the secondary goldmine and 0.962 mg/kg in the primary goldmine. This agrees with the work of Rufus et al. (2007) which reported that shoot cadmium levels are usually less than 1 mg/kg. Similarly, arsenic and Zn reported in the shoots were much higher than the lower limits for normal metal concentration in plant leaves (Alloway and Ayre, 1993); this was close to the 1.3 mg/kg arsenic reported by Matschullat (2000) for ferns grown on unpolluted soils. Although other metals (Cd, Cu, and Cr) also recorded average values slightly above the lower limit for normal metal concentration in plant leaves (Alloway and Ayre, 1993), it could be said that though the shoot was contaminated with these metals, however, most of the metals were not present at concentration levels considered toxic to the plants. When the average values of these metals were compared with the toxicity range (Alloway and Ayre, 1993), the values recorded in this study were much less, except for Cu (21 mg/kg) which was present at toxic level in the primary goldmine, as this conforms with the range of 20 to 30 mg/kg suggested by Marschner (1995) as a general critical concentration for Cu toxicity. Although copper is an essential micronutrient, exposure to excess Cu has a detrimental effect on plant growth, the effect being largely on root growth and morphology (Marschner, 1995). Thus, copper toxicity is considered a problem of significance to both the agricultural and environmental sector and the sources of copper contamination include mining and smelting, urban industrial and agricultural wastes/ use of agrochemicals.

Consequently, from the calculated bioaccumulation factor in this study, it was observed that the values for most of the metals were less than 1 in the secondary goldmine, except for As (1.01). However, the bioaccumulation factor were greater than 1 for Cd (1.15), Cu (2.06), Zn (2.42) and As (1.07), while Pb (0.29), Cr (0.13) and Co (0.18) had lesser values in the primary goldmine goldmine. This agrees with the findings of Pitchel et al. (1999) in which they suggested that with the exception of mercury, metal uptake into roots occurs from the aqueous phase, therefore in soil metals such as Zn and Cd, occur primarily as soluble or exchangeable readily bioavailable form, while others such as Pb occur as insoluble precipitates (that is, phosphates, carbonates and hydroxyl-oxides) which are largely unavailable for plant uptake. It is also believed that the availability factor recorded for Zn could be a reflection of availability of the high Zn recorded for soil in the primary goldmine. Also the bioconcentration/ availability factor (that is, average arsenic concentration in soil), was higher than the average recorded in the plant for the two locations studied, this could be as a result of the conditions stated by Pitchel et al. (1999).

Furthermore, the shoot: root ratio which also represents the translocation factor (TF) for the plant was calculated as described by Brooks (1998), this showed that Cd, Cu, As, Zn, Cr and Co had values >1 with exception of Pb having value less than 1 for the secondary goldmine location, while in the primary goldmine Cr and Co had TF values <1. Previous works have reported that Zn and Cd have high translocation factor which is a reflection of their relatively poor sorption in the soil (Mendez et al., 2007), while metals such as Cr, Co and Pb have low coefficients because they are usually strongly bound to the soil colloids (Kloke,1980). This result is in concordance with the report of Rufus et al. (2007), in which it was said that a plant must have the ability to translocate elements from roots to shoots at high rates. It also agrees with the works of Brown et al. (1995) and Li et al. (1996), who suggested that normally, Zn, Cd concentrations in plant roots are 10 or more times higher than shoot concentrations, but in hyper-accumulators, shoot metal concentrations can exceed root levels. This implies that the plants (aquatic ferns) used in this study could be considered for phyto-extraction of metals especially Cu, Co and Cr in the secondary goldmine and Cd, Pb and Zn in the primary goldmine (that is, metals which had highest translocation factor) but not for phyto-stabilization (Brooks et al., 1998).

Conclusion

This study was conducted to assess the metal contamination in the soils and plants from primary and secondary abandoned gold mines. The following conclusions were reached:

1. In the soils, the trend of metal concentration was, Cr >Zn >Cu >Co >Pb >As >Cd. Soils in the secondary goldmine has mean values for Cu, Cr and Co higher than NCI standards for soil (Kloke, 1980), which is indicative of Cu, Cr Co contamination in general; while chromium concentration of 79.4 mg/kg was observed in the soils of the secondary goldmine indicating chromium toxicity, at both 0 to 15 cm and 15 to 30 cm depths. Soils in the primary goldmine still had normal concentrations for the metals studied; notably, the 15 to 30 cm depth had a higher load of the metals compared to the 0 to 15 cm, indicating that erosion and leaching pose an effect in the movement of the metals down to the water bodies and down the profile respectively.
2. The trend in plants for metal concentration was Zn >Cu >Pb> Cr >Co >As >Cd >Cd. Cd. Cu and Zn contamination in plants from the primary goldmine, being above the normal concentration of metals found in plants (1 to 40 and 5 to 20 mg/kg for Zn and Cu respectively); though Cu was considered to be present at toxic level in the primary goldmine (21 mg/kg). Furthermore, the plants considered in this study (aquatic ferns), were observed to have high potential for phytoextraction of metals (that is, Cu, Co and Cr) in the secondary goldmine and (Cd, Pb and Zn) in the primary goldmine.

REFERENCES

Actlabs (Activation laboratory, Ontario Canada). (2008). Retrieved from http:// www. actlabs.com, accessed on 7th July.

Actlabsint (activation laboratories international). (2009). Retrieved from http://www.actlabls int.com, accessed on 23rd march.

Ahumada I, Escudero P, Ascar L, Richter JMP (2007). Extractability of Arsenic, copper and load in soils of mining and agricultural zone in central Chile. Commun. Soil Sci. Plant Anal. 35 (11&12):1615-1634.

Alloway BJ, Ayres DC (1993). Chemical principles of environmental pollution. Blackie academic and professional, Glasglow

Aslibekian O, Moles R (2003). Environmental risk assessment of metals contaminated soils at silver mines abandoned mine site, co tipperary, Ireland. Environ. Geochem. Health 25:247-266. (Pub Med)

Audu AA, Lawal AO (2005). Variation in metal contents of plants in vegetable gardens sites in Kano metropolis. J. Appl. Sci. Environ. Manage. 10:105-109.

Baker DE (1990). Copper. In: Alloway, B.J. (Ed.) Heavy metals in soils. New York: John Wiley. pp. 151-196

Brooks RR (1998). Plants that hyperaccumulate heavy metals. Theirrole in phytoremediation, microbiology, archeology, mineral exploration and phytomining Wallingford, UK. CAB International. p. 380.

Brown SL, Chaney RL, Angle JS, Baker AJM (1995). Zinc and Cadmium uptake of Thalspi caerulescens grown in nutrient solution. Soil Sci. Am. J. 59:125-133.

Carter MR, Gregorich EG (1994). Soil sampling and method of analysis. p.99, accessed on www.amazon.com.

Chung JH, Kang PS, Kim CY, Lee KS, Hwang TY, Kim GT, Park JS, Park SY, Kim DS, Lim OT, Sakong J (2005). Blood Pb, urine Cd and health assessment of residents in the vicinity of abandoned mines in Gyeongsangbuk-do. Korean J. Occup. Environ. Med. 17:225-237.

Das P, Samantary S, Rout GR (1997). Studies on cadmium toxicity in plants: A review. Environ. Pollut. 98:29-36.

Diatta J, Grzebisz W, Apolinarska.K (2003). A study of soil pollution by heavy metals in the city of Poznan (Poland) using Dandelion (Taraxacum officinale WED) as a bioaccumulator, EJPAU 6(2):01.

Faruk O, Nazim S, Kara SM (2006). Monitoring of cadmium and micronutrients in spices commonly consumed in Turkey. Res. J. Agric. Biol. Sci. 2:223-226.

Kabata-Pendias A (1995). Agricultural problems related to excessive trace metal contents of soil, in Heavy metals (problems and solutions)"", Ed.W. Salomons, U. Forstener and P mader), springer verlag, Berlin, Heiidelberg, new York, London, Tokyo. pp. 3-18.

Kloke A (1980). Richwerte 80, orientierungsdaten fur tolerierbare gesamtgehalte einiger elemente in kulturboden, mitt, VD LUFA, H. 2:9-11.

Li YM, Chaney RL, Angle JS, Chen KY, Kerschner BA, Baker AJM (1996). Genotypical in Zinc and Cd hyperaccumulation in Thlapsi caerulescens [abstract]. Agronony Abstract. p. 27.

Ma LQ, Komar KM, Tu C, Zhang WH, Cai Y, Kennelly ED (2001). A fern that hyperaccumulates arsenic. Nature 409:579.

Marschner H (1995). Functions of mineral nutrients: micronutrients. In mineral nutrition of higher plants. 2nd ed. Academic press limited, San Diego, CA. pp. 313-396.

Matschullat J (2000). Arsenic in the geosphere. A Rev. Sci. Total Environ. 249:297-312.

McBride M, Sauve S, Hendershot (1997). solubility control of Cu, Zn, Cd and Pb in contaminated soils. Eur. J. Soil Sci. 48: 337-346.

Mendez MO, Glenn EP, Maier RM (2007). Phytostabilization potential of quailbush for mine tailings. growth, metal accumulation, and microbial community changes. J. Environ. Qual..36:245-253

Nelson DW, Sommers LE (1982). Total carbon, organic matter. pp. 539-580. In Page, A.L et al., (ed) methods of soil analysis. Part 2. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

NMC, (Nigerian Mining Corporation). (1987). Mining industry of Nigeria retrieved from http://en.wikipedia.org/ wiki /mining_ industry_ of_Nigeria.

Nyangababo JT, Hamya JW (1985). The deposition of lead, cadmium, Zinc and copper from motor traffic on Brachiaria enimii and soil along a major Bombo road in Kampala city. Int. J. Environ. Stud. 27:115-149.

Park JD, Park CH, Choi BS, Kang EY, Hong YP, Chang IW, Chun BY, Yeh MH (1998). A study on urinary cadmium concentration and renal indices of inhabitant in an abandoned mine area. J. Prev. Med. Public Health 31:424-439.

Pitchel J, Kuroiwa K, Sawyer HT (1999). Distribution of Pb, Cd and Ba in soils and plants of two contaminated soils. Environ. Pollut. 110:171-178.

Porebska G, Ostrowska A (1999). Heavy metal accumulation in wild plants. implications for phytoremediation Polish J. Environ. Studies , 8 (6): 433 – 442. 00-548 Warsaw, Poland.

Romheld V, Marschner H (1986). Mobilization of iron in yhe rhizosphere of different plant species. Adv. Plant Nutr. 2:155-204.

Rana L, Dhankhar R, Chhikara S (2010). Soil characteristics affected by longterm application of sewage waste. Int. J. Environ. Res. Univ. Tehran. 4(3):513-518.

Rufus L, Chaney RL, Minie M, Yin Ml, Sally LB, Eric PB, Angle JS, Baker AJM (2007). Phytoremediation of soil metals, department of Agriculture – agric. Research Service, Beltsville.

Thomas GW (1982). Exchangeable cations.. *In:* A.L. Page et al. (ed.) Methods of soil analysis: Part 2. Chemical and microbiological properties. ASA Monograph 9:159-165.

TML (Tropical Mines Limited) (1996). A pre-investment study of the primary goldmine-odo Ijesa (primary) gold deposit report (2): 1-12.

Wang QR, Cui YS, Liu XM, Dong YT, Christie P (2003). Soil contamination and plant uptake of heavy metals at polluted sites in China. J. Environ. Sci. Health A Toxic. Hazard Subst. Environ. Eng. 38(5):823-38.

Wikipedia (2007). Gold. Retrieved from http//en.wikipedia.org/wiki/gold. 20 November. wikipedia foundation, inc.

Wikipedia (2008). Goldmining. Retrieved from http//en.wikipedia.org/wiki/Gold_mining. 4 November.