

Full Length Research Paper

Heavy metal pollution around Itakpe mine, Kogi State, Nigeria

Kakulu Samuel and Matthews-Amune Omono Christiana*

Department of Chemistry, University of Abuja, Abuja, Nigeria.

Accepted 22 May, 2012

The removal of large quantities of overburden through mining has resulted in the pollution of various ecosystems. Soil pollution around the Itakpe mine in Kogi State, Nigeria was studied through the determination of heavy metal concentration and chemical speciation of the metals cadmium (Cd), copper (Cu), magnesium (Mg), nickel (Ni), lead (Pb) and zinc (Zn) in soil using Flame Atomic Absorption Spectroscopy. Soil digestion was done with hydrofluoric-perchloric (HF-HClO₄) acid mixture (5:1) and sequential extraction was carried out with different reagents in the extraction steps; Exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and residual. Mean metal content of mining site soil is 0.16±0.02, 0.15±0.03, 0.04±0.02, 0.11±0.02, 0.07±0.01 and 0.04±0.03 µg/g for Cd, Cu, Mg, Ni, Pb and Zn, respectively. Results of sequential extraction of the mining site soil show that the highest metallic levels were observed in the Fe-Mn, organic and residual fractions.

Key words: Mine, heavy metals, tailings, pollution, agricultural soil.

INTRODUCTION

Mining, which is a major source of anthropogenic introduction of metals into the environment, is an important part of many countries economies (Bridge, 2004; Arogunjo, 2007; Nriagu, 1992). Mining processes lead to the removal of large quantities of overburden waste materials whose constituent vary from mine to mine and are a function of mineral substances extracted from the earth surface in which extraction took place (Arogunjo, 2007; Stephanic, 1998; Richtera et al., 2004; Ameh and Akpah, 2011). Environmental effects of mining depend on how well the displaced material is managed. According to a WHO report in most developing countries small-scale or surface mining results in mining activities affecting health through method of extraction which contaminates the environment (Chhotu et al., 2009).

Mining of ores and other mining processes result in the metal being released from its stable form into the environment (Nriagu, 1992; Stephanic, 1998; Jarup, 2003). This leads to metals scattering in the mine surroundings

(Arogunjo, 2007; Duruibe et al., 2007; Nriagu, 1992; Stephanic, 1998; Jian-Min et al., 2007). These tailings are continuously dispersed through erosion, wind action and effluent draining the waste into arable land, rivers and ground waters polluting air, soil, vegetation, surface and ground waters, changing or destroying aquatic habitats, affecting agricultural lands, and causing health problems to humans (Nriagu, 1992; Stephanic, 1998; Duruibe et al., 2007; Ameh and Akpah, 2011; Jian-Min et al., 2007). Pollution from mining has also been reported to come through chemicals used for mineral processes such as Hg and CN (Arogunjo, 2007; Duruibe et al., 2007; Lin et al., 2005; Lee et al., 2001). There is occurrence of acid mine drainage (AMD) when sulphur ores are mined and this is reported to take metals into solution contaminating water bodies with serious effects on aquatic life (Arogunjo, 2007; Jian-Min et al., 2007; Jung, 2001).

Thus studies show that mining and related operations contaminate the environment with metals, ruins ecosystems through barren land, polluting water, altering soil/sediment constituent, alteration of drainage patterns, denude forests and so on (Nriagu, 1992; Stephanic, 1998; Jian-Min et al., 2007; Ameh and Akpah, 2011; Lee et al., 2001). Mining processes also enhance metal burden

*Corresponding author. E-mail omonomatthews@yahoo.com.
Tel: +23408035975950.

in mine workers and other inhabitants of the mining environment (Duruibe et al., 2007; Stephanic, 1998; Nriagu 1992; Ameh and Akpah, 2011). Heavy metals uptake by plants and successive accumulation in human tissues and biomagnifications through the food chain causes both human health and environment concerns.

Heavy metals are reported to remain in soils even after their addition to soils have been stopped (Lee et al., 2001; Nriagu, 1992; Rao et al., 2008). Research has shown that the total heavy metals in soil is partitioned over fractions; exchangeable, carbonates, oxides of Fe and Mn, organic matter and aluminosilicates with oxides of Fe and Mn reported to harbour the highest levels of available heavy metals (Hlavay et al., 2004; Jian-Min et al., 2007; Lin et al., 2005; Pendas and Dubka, 1992; Rao et al., 2008). Of the greatest concern are the metals retained in the form of exchangeable, which may occur in the form of oxide, hydroxide, carbonate and/or bonded to organic matter depending on soil condition because these are the forms that are readily available to plants (Hlavay et al., 2004; Lin et al., 2005).

Various studies on mining and its effects have been carried out in the UK, US and several other countries with limited studies undertaken in Nigeria. Mining activities in the vicinity of the Dabaoshan Mine in China for example is reported to have polluted 83 villages, 585×10^4 m² paddy fields and 21×10^4 m² ponds (Jian-Min et al., 2007). Mining activities in Nigeria constitute environmental pollution and land degradation because in most mining sites unregulated mining activities are operational leading to indiscriminate dumping of industrial waste (Nriagu, 1992; Stephanic, 1998). The Itakpe iron ore deposit in Nigeria have been reported to release Ti, Cr, Mn, Cd, Ta, Ca, Zn, Cu into the environment (Arogunjo, 2007).

With industrialization and agriculture increasing the presence of heavy metals in our environment, and their presence in food crops and most edibles, there is an increasing need to study heavy metal distribution and accumulation in soils. The aim of the present work is to determine the concentration of some heavy metals in soils and determine speciation of metals in the soil to access their toxicity.

MATERIALS AND METHODS

All reagents used were analytical grade (BDH, Poole, England) and were used without further purification. All glassware were washed with detergent, rinsed with distilled water, soaked in 10% HNO₃ for 24 h and rinsed. Atomic Absorption Spectrophotometer (AAS) model 210VGP, Buck Scientific Incorporated USA was used for the determination of heavy metals that were studied and Thermo Scientific ARL 9,000 X-ray Work Station was used for X-ray fluorescence studies.

Figure 1 shows map of Itakpe with sampling points. A total of 60 soil samples were collected using a stainless steel knife from the upper 15 cm layer from farm during the dry season (January 2010) and wet season (July 2010) in the mine area (L6), beneficiation plant area (L7) and control farm (L8) in Osara Dam area-12 km from

Itakpe. Soil samples were collected in nylon bags previously soaked in 10% HNO₃ solution for 24 h, rinsed with deionized water and air dried. The collected samples were air-dried for seventy-two hours, ground in a mortar and passed through 2 mm sieve and 0.005 mm and stored in clean polythene bags.

Tessier et al. (1979) sequential extraction and total metal content procedure was used to determine the fractionation of the studied metals.

A. Sequential extraction:

1. The fraction exchangeable: 1 g (< 2 mm) soil sample, 8 ml of 1 M MgCl₂ (pH 7), 1 h, continuous agitation, room temperature,
2. The fraction bound to carbonates: 8 ml of 1 M NaOAc (pH 5 with HOAc), 5 h continuous agitation, room temperature.
3. The fraction bound to Fe and Mn-oxides: 20 ml of 0.04 M NH₂OH.HCl in 25% (v/v) HOAc (pH 2), 6 h at 96±3°C with occasional agitation.
4. The fraction bound to organic matter: 3 ml of 0.02 M HNO₃ and 5 ml of 30% H₂O₂ (pH 2 with HNO₃) at 85±2°C, 2 h, occasional agitation. A second 3 ml 30% H₂O₂ (pH 2 with HNO₃), 85±2°C, 3 h, occasional agitation, cooling, 5 ml of 3.2 M NH₄OAc in 20% (v/v) HNO₃, diluted to 20 ml with 5 ml H₂O, agitated continually for 30 min, 3.2 M NH₄OAc.
5. Residual: The residue from (4) was digested with a HF-HClO₄ mixture according to the procedure for Total metal analysis.

The extraction solution was centrifuged after each extraction step and the supernatant removed by filtration into a plastic bottle. Two drops of HNO₃ was added to sample. Sample was kept for AAS analysis. The residual soil sample was shaken in 8 ml of deionized water, after each extraction, centrifuged and the supernatant discarded.

B. Total metal analysis procedure was carried out by digesting 1 g (<0.005 mm) of soil sample with a mixture of 10 ml HF and 2 ml HClO₄ to near dryness; a second addition of 10 ml HF and 1 ml HClO₄ was made and again the mixture was evaporated to near dryness. Finally 1 ml HClO₄ alone was added and the soil sample evaporated until the appearance of white fumes. The residue was dissolved in concentrated HCl and diluted to 25 ml. The resulting solution was filtered into a plastic bottle ready for AAS.

Assessment of accuracy and precision was done through using three replicate samples, quality control system (international standard reference material-Soil Reference Material 989, Wageningen Evaluating Programs for Analytical laboratories (WEPAL), Netherland), spiking of plant samples and reagent blanks.

RESULTS

X-ray analysis of the studied soils is shown in Table 1. The mining site soil is high in silica mixed with oxides of Mg, Ca, Fe, Al, K, Na and S. The concentration of heavy metals in dry and rainy season soil is shown in Table 2. Generally the metal levels were low. There was no specific variation pattern between the rainy season metal levels and the dry season levels. Total soil concentration of Cd ranged from 0.14 to 0.18, Cu ranged from 0.13 to 0.16, Mg ranged from 0.04 to 0.04, Ni ranged from 0.07 to 0.15, Pb ranged from 0.06 to 0.07 and Zn ranged from 0.04 to 0.04 µg/g. The total soil metal level for Mg was the same for both seasons. Zn and Pb levels were relatively low (Zn, from 0.04 to 0.04 and Pb, from 0.06 to

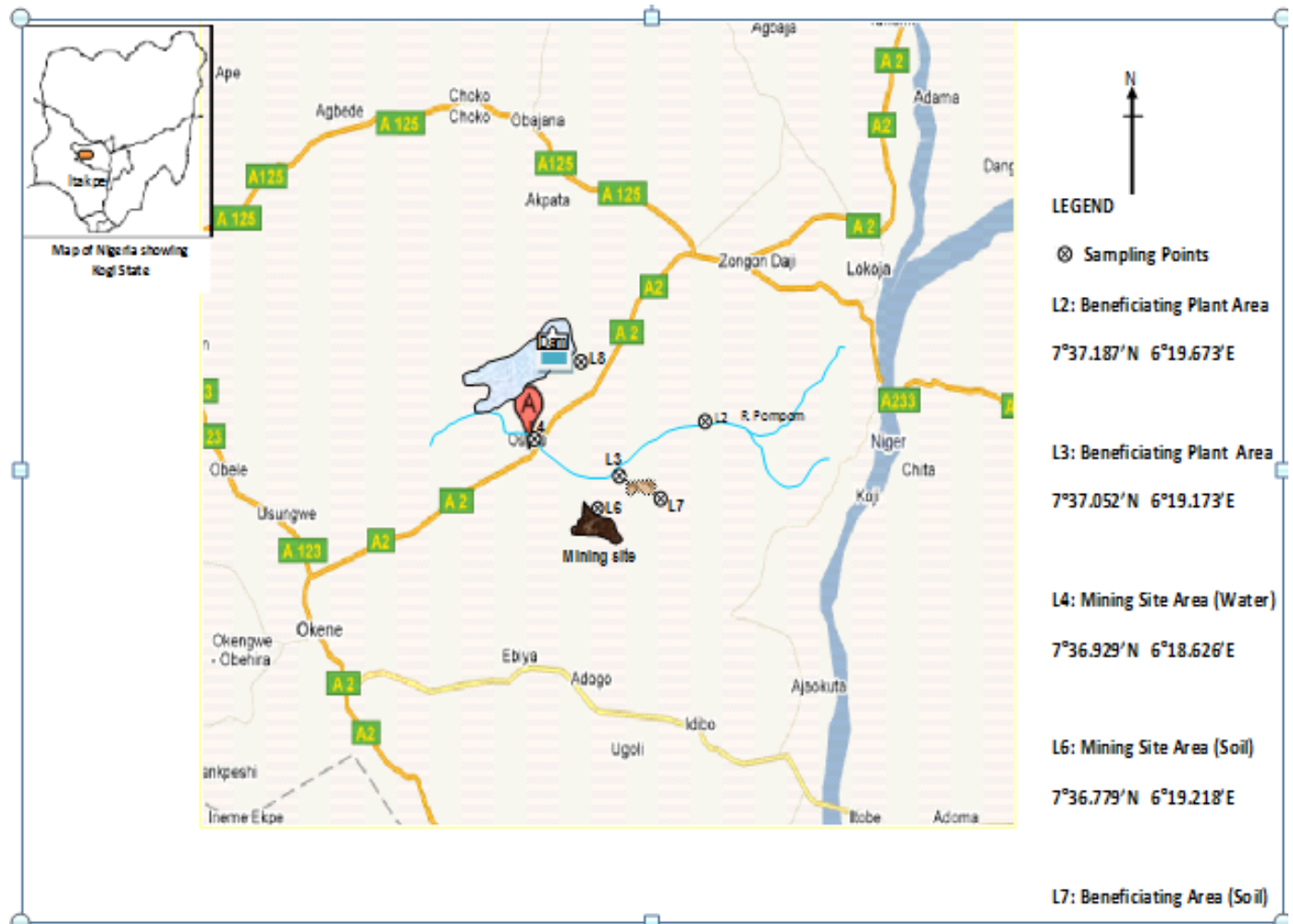


Figure 1. Map of Itakpe mining environment showing sampling areas.

Table 1. X-ray analysis of the studied soils (%).

Metal oxide	Mining site	Control
SiO ₂	77.59	78.00
Al ₂ O ₃	6.72	2.56
Fe ₂ O ₃	11.24	4.26
CaO	0.27	0.23
MgO	0.15	0.06
K ₂ O	1.36	0.23
Na ₂ O	0.49	0.08
SO ₂	0.02	0.03

0.07 µg/g). The total metal levels in the control soil were relatively lower than the mining site soil.

The percentage of heavy metals in the soil fractions is shown in Table 3. The mean percentage value for Cd in the soil fractions range from 8.29 to 33.47, Cu from 12.04 to 32.57, Mg from 7.89 to 36.28, Ni from 3.67 to 44.32,

Pb from 5.10 to 34.767 and Zn ranged from 8.29 to 30.63%. Cd was highest in the Fe-Mn oxide fraction (36.15% of control) and lowest in the organic fraction of the control soil (2.55%), Cu was highest in the carbonate fraction of control soil (32.95%) and lowest in the organic and residual fraction of control soil (8.59%), Mg was

Table 2. Concentration of heavy metals in dry and rainy season soils \pm SD ($\mu\text{g/g}$).

Metal	Mining site			Control
	Dry season	Rainy season	Mean Conc.	
Cd	0.14 \pm 0.01 (0.17-0.18) ^a	0.18 \pm 0.02 (0.12-0.15) ^a	0.16 \pm 0.02 (0.14-0.18) ^a	0.10 \pm 0.01 (0.09-0.11) ^a
Cu	0.16 \pm 0.03 (0.08-0.18) ^a	0.13 \pm 0.03 (0.14-0.17) ^a	0.15 \pm 0.03 (0.12-0.18) ^a	0.07 \pm 0.01 (0.06-0.08) ^a
Mg	0.04 \pm 0.002 (0.04-0.04) ^a	0.04 \pm 0.002 (0.04-0.04) ^a	0.04 \pm 0.02 (0.01-0.05) ^a	0.03 \pm 0.003 (0.027-0.033) ^a
Ni	0.07 \pm 0.01 (0.05-0.09) ^a	0.15 \pm 0.03 (0.13-0.17) ^a	0.11 \pm 0.02 (0.08-0.12) ^a	0.01 \pm 0.01 (0.00-0.02) ^a
Pb	0.06 \pm 0.02 (0.05-0.07) ^a	0.07 \pm 0.004 (0.06-0.07) ^a	0.07 \pm 0.01 (0.06-0.08) ^a	0.02 \pm 0.001 (0.017-0.021) ^a
Zn	0.04 \pm 0.05 (0.04-0.04) ^a	0.04 \pm 0.03 (0.03-0.04) ^a	0.04 \pm 0.03 (0.00-0.08) ^a	0.03 \pm 0.01 (0.02-0.04) ^a

a = range.

Table 3. Mean % of heavy metal in soil fractions.

Fraction	Mining site					
	Cd	Cu	Mg	Ni	Pb	Zn
F1	12.64 \pm 0.78	12.09 \pm 0.82	7.89 \pm 0.78	3.67 \pm 0.31	13.36 \pm 2.29	9.03 \pm 1.22
F2	23.50 \pm 1.34	12.44 \pm 0.47	12.10 \pm 0.34	6.20 \pm 0.66	5.10 \pm 2.176	8.29 \pm 2.92
F3	22.62 \pm 7.08	32.57 \pm 6.82	22.50 \pm 1.95	15.32 \pm 1.60	17.24 \pm 1.64	29.85 \pm 7.00
F4	8.29 \pm 0.98	30.41 \pm 9.09	21.25 \pm 3.65	30.51 \pm 3.60	29.51 \pm 6.15	29.85 \pm 1.45
F5	33.47 \pm 1.92	12.04 \pm 4.47	36.28 \pm 3.30	44.32 \pm 2.05	34.76 \pm 3.15	30.63 \pm 5.10
	Control					
	Cd	Cu	Mg	Ni	Pb	Zn
F1	16.49 \pm 1.63	17.79 \pm 0.41	7.32 \pm 0.67	2.43 \pm 0.21	6.91 \pm 0.51	18.09 \pm 3.18
F2	19.32 \pm 4.95	32.95 \pm 6.07	14.22 \pm 5.23	5.86 \pm 0.62	6.11 \pm 2.16	7.58 \pm 2.85
F3	36.15 \pm 2.53	23.22 \pm 7.52	19.85 \pm 1.71	28.15 \pm 1.1	28.15 \pm 3.6	26.36 \pm 13.2
F4	2.55 \pm 0.20	8.59 \pm 0.15	25.52 \pm 2.54	49.27 \pm 0.7	19.46 \pm 0.7	30.42 \pm 0.71
F5	25.49 \pm 1.66	8.59 \pm 0.15	27.36 \pm 3.90	22.58 \pm 1.2	39.36 \pm 3.6	17.55 \pm 1.47

F1= Exchangeable, F2 = carbonates, F3 = Fe-Mn oxide fraction, F4 = organic fraction, F5 = residual fraction.

highest in the residual fraction of mining site soil (36.28%) and lowest in the exchangeable fraction of control soil (7.32%), Ni was highest in the residual fraction of mining site soil (44.32%) and lowest in the control soil (2.43%), Pb was highest in the organic fraction of control soil (39.36%) and lowest in the carbonate fraction of mining site soil (5.10%), Zn was highest in the residual fraction of the mining site soil (30.63%) and lowest in the carbonate fraction of control

soil (7.58%).

DISCUSSION

The X-ray studies on the soil sample (Table 1) shows all metals to be present in the oxide forms with Si, Al, Fe, Ca and Mg metals present as part of the soil components. Metals from anthropogenic sources are reported to occur

in the form of oxides, sulphides and carbonates and the larger part of toxic elements of industrial origin were reported to be mainly from the oxides, and a lesser part from the sulphides (Ekosse et al., 2005; Hesterberg, 1998). The results obtained show that sand fraction was the dominant parameter of Itakpe mining environment soil. According to Ekosse et al. (2005), transportation of heavy metals in soils favours sandy soils compared to clayey and silty soils. The presence of SO₂ is in agreement with previous report that soil in the area of industrial influence can be contaminated by acid-forming compounds such as SO₂ which enter the atmosphere (Sulkowski and Hirner, 2006). Oxidants in mining environment are reported to influence the physiochemical properties of the soil (Ekosse et al., 2005; D'Elia et al., 1999). There is also the possibility of oxidation of metal sulphides causing release of metals to the environment (Lin et al., 2005; Zhou et al., 2007). This could contribute to the contamination level of the soils in the vicinity of the Itakpe mining environment.

Results show mean metal content of mining site soil (Table 2) to be 0.16±0.02, 0.15±0.03, 0.04±0.02, 0.11±0.02, 0.07±0.01 and Zn 0.04±0.03 µg/g for Cd, Cu, Mg, Ni, Pb and Zn respectively. The metallic levels were observed to be relatively low. These levels are lower than the normal soil content intervals, maximum allowable limits of heavy metals in soils and are below the maximum levels reported from various countries for agricultural use based on soil quality guidelines (Pendias and Dubka, 1992; Bero and Reaves, 1984; Adie and Osibanjo, 2009).

Metallic contaminants from the mining environment can be dispersed and transported downstream through atmospheric processes such as wind with the extent of metal removal depending on factors such as mineralogy of tailings, total metal concentration and their speciation, physiochemical properties of solution and the presence or absence of competing ions (Jung, 2001, 2008; Jian-Min et al., 2007; Zhou et al., 2007). These contaminants are further transported through erosion into agricultural soils, food crops and water bodies polluting them (Bridge, 2004; Jung, 2008; Jian-Min et al., 2007).

Table 1 show that the metallic levels of the mining site soil were higher in both seasons than the level in the control farm. However anomalies in metallic levels could occur as a result of heavy metal deposition on soil surface from various sources through atmospheric transportation (Ukpebor and Unuigbo, 2003). The studied metals had no specific patterns of distribution during both seasons. However there were variations which could be due to changes in physicochemical properties of agricultural soils during the rainy season (Adie and Osibanjo, 2009; Giacomino et al., 2010; Zimmerman and Weindorf, 2010; Lee et al., 2001). Effects such as erosion due to floods results in uneven distribution of metals in certain part of the farm where the topography is sloppy and dissolution of carbonates and oxides (Cebula and Ciba,

2005; Lee et al., 2001; Pravin et al., 2010; Hesterberg, 1998; Hlavay et al., 2004; Adie and Osibanjo, 2009). Effects of change in soil properties within a short distance can result in changes in metal solubility, non-equilibrium distribution of water and microbial mediated processes (Hesterberg, 1998; Hlavay et al., 2004; Adie and Osibanjo, 2009).

Result of the fractioning of the mining site soil is shown in Table 2. Variations in toxicity of a metal is related to variations in soil properties and seasonal changes which modifies the speciation of a metal and, thereby, its bioavailability (Jian-Min et al., 2007). The percentage of the studied metals Cd, Cu, Mg, Ni, Pb and Zn present in the exchangeable and carbonate fractions were observed to be low except Cd 23.50±1.34% in mining site soil, Cu 32.95±6.07% and Cd 19.32±4.95% in control soil of the carbonate fraction in all the soils during both seasons and were relatively lower than those in the other fractions (Table 2). Such report on low levels in these fractions has been given by previous researchers (Jung, 2008; Ameh and Akpah, 2011; Rao et al., 2008). This disagrees with other researchers who reported high concentration level in the exchangeable fraction. Jung and Thornton (1997) reported level as high as 30% of Cd in exchangeable fraction while Jian-Min et al. (2007) reported high levels of metals in the carbonate fraction.

The highest levels of metal concentrations in both soils were observed in the Fe-Mn oxide, organic and residual fractions. This disagrees with the report of previous researchers that the Fe-Mn oxide fraction stores the highest level of metals. (Richtera et al., 2004), Ameh and Akpah (2011), Tessier et al. (1979), Hesterberg (1998), D'Elia et al., 1999) Cu was mainly bound to the Fe-Mn oxide fraction (32.57±6.82%) in the mining site soil. This is in agreement with previous research that Cu accumulates on underlying iron hydroxide (Adie and Osibanjo (2009). This disagrees with Wong et al. (2002) report that there is strong association between soil Cu and the organic fraction. Cd of control soil was highest at the Fe-Mn, oxide fraction (36.15±2.53%). Ni levels were relatively high in both soils (30.51±3.60% in organic fraction and 44.32±2.05% in residual fraction of mining site soil and 49.27±0.70% of the organic fraction of control soil). Zn levels were highest in the residual fraction of mining site soil farm but highest in the organic fraction of control soil. This disagrees with previous report that majority of Zn is found in the residual fraction. (Rao et al. (2008), Wong et al., 2002) Pb levels were observed to be highest in the residual fractions of both soils. This disagrees with the report of Wong et al. (2002) There are reports that Pb is largely associated with the Fe-Mn oxide and residual fractions. (Adie and Osibanjo (2009), Wong et al., 2002) According to Wong et al. (2002) there is strong association between Pb and the Fe-Mn oxide and organic fractions. This shows that Pb is relatively stable after deposition in soils. Such reports have been given by Jian-Min et al. (2007) and Adie and Osibanjo,

2009).

The relatively high levels observed in the organic fraction Cu 30.41 ± 9.09 , Ni 30.51 ± 3.60 , Pb 29.51 ± 6.15 and $29.85 \pm 1.45\%$ for Zn in mining site soil and Ni $49.27 \pm 0.70\%$ and Zn $30.42 \pm 0.71\%$ of control soil could be due to the oxidation of Sulphide ores and the decomposition of organic matter under oxidizing condition to release metals. Such observations have previously been reported (Jian-Min et al., 2007; Zhou et al., 2007; Rao et al., 2008). The high levels observed in the Fe–Mn Oxide fraction Cu $32.57 \pm 6.82\%$ and Zn $29.85 \pm 7.00\%$ of the mining site soil and Cd 36.15 ± 2.53 , Ni 28.15 ± 1.10 , Pb 28.15 ± 3.60 and Zn $26.36 \pm 13.2\%$ could be as a result of reduction of the oxides which could cause metals to be released. According to Jian-Min et al. (2007) under reducing conditions metals present in the Fe–Mn Oxide fraction are unstable and are easily released through dissolution releasing soluble metals. This implies that the potential risks of metal pollution will increase with time. (Jian-Min et al., 2007) The high levels of metals observed at the residual fraction Cd 33.47 ± 1.92 , Mg 36.28 ± 3.30 , Ni 44.32 ± 2.05 , Pb 34.76 ± 3.15 and Zn $30.63 \pm 5.10\%$ of mining site soil and Cd 25.49 ± 1.66 , Mg 27.36 ± 3.90 and Pb $39.36 \pm 3.60\%$ indicates that these metals are bound to the primary and secondary minerals.

Analysis of variance (ANOVA) report has significant difference ($p < 0.05$) in all the studied metals. This shows that all the studied metals at the different levels were not uniformly distributed in all the fractions. This could be due to the different rates of retention of these metals in the soil.

Conclusion

The metallic levels of the soil in the Itakpe mining environment soil is not highly contaminated based on the concentration levels (0.16 ± 0.02 , 0.15 ± 0.03 , 0.04 ± 0.02 , 0.11 ± 0.02 , 0.07 ± 0.01 and 0.04 ± 0.03 $\mu\text{g/g}$ for Cd, Cu, Mg, Ni, Pb and Zn) of the metals. These metallic levels of the studied metals are below the maximum levels reported from various countries for agricultural use based on soil quality guidelines. The highest levels of metal concentrations in both soils were observed in the Fe–Mn oxide, organic and residual fractions. Under certain environmental conditions metals present in these fractions become unstable and are easily released through dissolution. This implies that the potential risks of metal pollution will increase with time. Hence there is need for regular monitoring to safeguard the populace of Itakpe mining environment.

REFERENCES

- Adie GU, Osibanjo (2009). Assessment of soil-pollution by slag from an automobile battery manufacturing plant in Nigeria. *Afr. J. Environ. Sci. Technol.* 3(9):239-250.
- Ameh E, Akpah FA (2011). Heavy metal pollution indexing and multivariate statistical evaluation of hydrogeochemistry of River PovPov in Itakpe Iron-Ore mining area, Kogi State, Nigeria. *Adv. In Appl. Sci. Res.* 2(1):33-46.
- Arogunjo AM (2007). Heavy metal composition of some solid minerals in Nigeria: Any Health Implication to inhabitants around the Mining sites. *Int. J. Appl. Environ. Sci.* 2(2):143-153.
- Bero MI, Reaves GA (1984). Background Levels of Trace Elements in Soils; In *Proceed. Inst. Int. Conf. on Environmental Contamination CEP Consultants, Edinburgh, Scotland* pp. 333-340.
- Bridge G (2004). Contested Terrain: Mining and the Environment. *Ann. Rev. Environ. Resour.* 29:205-259.
- Cebula E, Ciba J (2005). Effects of flooding in southern Poland on heavy metal concentrations in soils. *Soil Use and Manag.* 21:348-351.
- Chhotu DJ, Fuleka MH (2009). Review: Phytoremediation of heavy metals: Recent Techniques. *Afr. J. Biotechnol.* 8(6):921-928.
- D'Elia V, Lodi V, Naldi M, Gherardi G, Violante FS, Bonparola M, Badiello R, Raff AG (1999). Gardening work and heavy metals in urban environment. *Arh hig rada toksik* 50(2):63-170.
- Duruibe JO, Ogwuebu MO, Egwurugwu JN (2007). Heavy metal pollution and human biotoxic effects. *Int. J. Phys. Sci.* 2(5):112-118.
- Ekosse GE, Ngila JC, Forchheh N (2005). Multivariable analyses of heavy metals in soils and *Colophospermum mopane* leaves around the Selebi Phikwe nickel-copper mine and smelter/concentrator plant area, Botswana. *J. Appl. Sci. Environ. Manag.* 9(1):177-185.
- Giacomino A, Malandrino M, Abollino O, Velayutham M, Chinnathangavel T, Mentasti E (2010). An approach for arsenic in a contaminated soil: Speciation. *Environ. Pollut.* 158(2):416-23.
- Hesterberg D (1998). Biogeochemical cycles and processes leading to changes in Mobility of chemicals in soil. *J. agric. Ecosyst. Environ.* 67:121-133.
- Hlavay J, Prohaska T, Weisz M, Wenzel WW, Stingeder GJ (2004). Determination of Trace Elements Bound to Soils and Sediment Fraction. *Pure Appl. Chem.* 76(2):415-442. (IUPAC Technical Report).
- Jarup L (2003). Hazards of heavy metals contamination. *Br. Med. Bull.* 68:167-182.
- Jian-Min Z, Zhi D, Mei-Fang C, Cong-Qiang L (2007). Soil Heavy Metal Pollution Around the Dabaoshan Mine, Guangdong Province, China. *Pedosph.* 17(5):588-594.
- Jung MC, Thornton (1997). Environmental contamination and seasonal variation of metals in soils, plants and waters in the paddy fields around a Pb–Zn mine in Korea. *Sci. Total Environ.* 198(2):105-121.
- Jung MC (2001). Heavy metal contamination of soils and waters in and around the Imcheon Au–Ag mine, Korea. *Appl. Geochem.* 16:1369-1375.
- Jung MC (2008). Heavy metal contamination in Soils and Factors Affecting Metal uptake by Plants in the Vicinity of a Korean Cu–W Mine. *Sensors.* 8:2413-2423.
- Lee CG, Chon H, Jung MC (2001). Heavy metal contamination in the vicinity of the Daduk Au–Ag–Pb–Zn mine, Korea. *Appl. Geochem.* 16(11-12):1377-1386.
- Lin C, Tong X, Lu W, Yan L, Wu Y, Nie C, Chu C, Long J (2005). Environmental impacts of surface mining on mind lands in the Dabaoshan Mine region, Southern China. *Land Degrad. Dev.* 16(5):463-474.
- Nriagu JO (1992). Toxic metal pollution in Africa. *Sci. Total Environ.* 121:1-31.
- Pendias PW, Dubka CM (1992). Background Levels and Environmental influence on trace metals in Soils of Temperate Humid Zone of Europe: In Adriano, Ed *Biogeochemistry of trace metals.* CRS Press. Boca Raton, Florida. pp. 61-64.
- Pravin U Singare RS, Lokhande, Pragati P, Pathak (2010). Soil Pollution along Kalwa Bridge at Thane Creek of Maharashtra, India *JEP*, 1 (2):121-128.
- Rao CRM, Sahuquillo A, Sanchez JFL (2008). A Review of the Different Methods Applied in Environmental Geochemistry For Single and Sequential Extraction of Trace Elements in Soil and Related Materials. *Water, Air Soil Pollut.* 189:291-333.
- Richtera P, Seguil R, Ahumada I, Cerdugo R, Narvz, J, Shibatac AY (2004). Arsenic Speciation in Environmental samples of mining impacted sector of Central Chile. *Chem. Soc.* 49(4):333-339.
- Stephanic J (1998). Major issues in miner health. *Environ. Health*

- Perspect. 106 (11)1.
- Sulkowski M, Hirner AV (2006).Element fractionation by sequential extraction in a soil with high carbonate content. *Appl. Geochem.* 21(1):16-28.
- Tessier A, Campell PGC, Bisson M (1979). Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Anal. Chem.* 51(7):844-851.
- Ukpebor EE, Unuigbe CA (2003). Heavy Metal Concentration in the Subsoil of Refuse Dumpsite in Benin City, Nigeria. *Ghanan J. Sci.* 43:9-15.
- Wong SC, Li XD, Zhang G, Qi SH, Min YS (2002). Heavy metals in agricultural soils of the Pearl River Delta, South China. *Environ. Poll.* 119(1):33-44.
- Zhou J, Dand Z, Cai M, Liu C (2007). Soil Heavy Metal Pollution around the Dabaoshan Mine, Guangdong Province, China. *Pedosph.* 17(5):588-594.
- Zimmerman AJ, Weindorf DC (2010). Heavy Metal and Trace Metal Analysis in soil by Sequential Extraction: A Review of Procedures. *Int. J. Anal. Chem.* Article, ID 387803, p. 7.