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Effect of Mining on Heavy Metal Concentration in Soils from the Vicinity of Itakpe Iron Ore Mine in Kogi State, Nigeria

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Abstract. The effects of mining on soils from Itakpe iron ore mining area in Kogi State, Nigeria were studied through the determination of the heavy metals (Cd, Cu, Mg, Ni, Pb and Zn) using flame atomic absorption spectroscopy. Soil samples were collected during the dry and rainy seasons. Significant levels of heavy metals were found. Median topsoil concentrations (0-15 cm) for Cd, Cu, Mg, Ni, Pb and Zn were 0.16±0.02, 0.15±0.03, 0.04±0.03, 0.1±0.02, 0.07±0.01, 0.04±0.04 µg/g, respectively. The heavy metal concentrations of control soil were relatively lower than those in the Itakpe mining environment soil and within levels of total metal contamination in the normal soil content intervals and maximum allowable limits of heavy metals in soils. Correlations analysis shows that heavy metals were closely correlated with each other except for Pb, indicating the studied metals are from the same pollutant resource. This shows, mining as contributing to the metallic levels in the Itakpe mining site.

Keywords: mining, heavy metals, soil, pollution

Introduction

The need for a country's economic, agricultural and industrial development acts as a challenge to safe and pure environment. These activities affect the natural and biological redistribution of metals through altering their chemical forms and introducing contaminants into the environment. (Ezeh and Chukwu, 2011; Aremua *et al.,* 2010; Wu *et al.,* 2010, Prathumratana *et al.,* 2008). The result is that metal pollutants are distributed in the atmosphere, water, soil and vegetation and could have long term hazardous impact on ecosystems. (Aremua *et al.,* 2010; Jung, 2008; Arogunjo, 2007). The greatest concerns are the heavy metals which are those with potential human and environmental toxicity accumulate in soils and induce pollution of food chain endangering the ecosystems safety and human health (Arogunjo, 2007; Ullrich *et al.,* 1999).

Heavy metals are persistent and have ability to bio-accumulate, transform to more toxic form, can neither be degraded nor destroyed and have average long-life (Arogunjo, 2007; Ukpebor and Unuigbe, 2003; Wong *et al.,* 2002). Some metals are essential trace element needed by organisms but the main threats to human health are associated with exposure to Pb, Hg, Cd and As; whose biotoxicity and occurrences require the knowledge of their sources, leaching processes, chemical conversions and modes of deposition to pollute the environment. (Ezeh and Chukwu, 2011; Yahaya *et al.,* 2009).

Chronic concentration or deficiency of these metals can have serious health effects varying from irritant to acute or chronic diseases, such as cancer, reproductive and nervous diseases, and so on. (Gutiérrez-Ginés, 2010; Arogunjo, 2007; Lin *et al.,* 2005).

Mining is needed to develop economic growth for many countries and it caused pollutant questions. Mining and metal processes activities which are major sources of anthropogenic pollution result in metals being released from their stable form into the environment. (Jung, 2008; Arogunjo, 2007). The Itakpe iron ore deposit in Nigeria is reported to release Ti, Cr, Mn, Cd, Ta, Ca, Zn, Cu into the environment while ore from Ipoti, Nigeria is reported to release Cd, (Arogunjo, 2007). Pollutants present in tailings and mine waste leads to metals scattering in the mine surroundings with their continuous disperse by soil erosion, wind action and effluent draining the waste into arable land, rivers and ground waters with change in climate leading to seasonal variations in their metallic levels. (Ameh and Akpah, 2011; Jung, 2008; Jian-Min *et al.,* 2007; Lin *et al.,* 2005).

With increase of industrialization and agricultural activities heavy metals are increasing in environment. Monitoring of bio available metals in polluted soils is

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threatening due to the presence of heavy metals in our environment, food crops and most edibles. Hence, there is an increasing need to study heavy metal distribution and accumulation in soils. The aim of this study was to determine the effect of iron mining on Itakpe mining soil, Nigeria by exploring the difference in the concentration of heavy metals from farm land, located in mining area and control sites. This study will help to target strategies for quality soil management.

Materials and Methods

The study area was Nigeria Iron Ore Mining Company, Itakpe in Okehi LGA of Kogi State in the North Central part of Nigeria. It lies within longitude 6° 16'E and latitude 7° 36'N. The residents are peasant farmers.

Figure 1 shows map of Itakpe with sampling points. A total of 75 soil samples were collected using a stainless steel knife from the upper 15cm layer during the dry season (DS) in January and rainy season (RS) in July 2010 in the Itakpe mining environment farms. Control soil samples were collected from Osara Dam Area 12 km away from Itakpe. Soil samples were collected in nylon bags previously soaked in 10% HNO_3 solution for 24 h, rinsed with deionized water and air dried. The collected soil samples were air-dried for 72 h, ground in a mortar and passed through 0.005 mm sieve and stored in clean polythene bags. All reagents used were of analytical grade (BDH, Poole, England). All glassware were washed with detergent, rinsed with distilled water, soaked in 10% HNO_3 for 24 h and rinsed.

Fig. 1a. Map of Nigeria showing Kogi State b, Map of Itakpe mining environment showing sampling areas.

Soil pH was determined using a soil-water ratio 1: 2.5 (w/v). Soil organic matter was determined using the Walkey-Black wet oxidation method. (Udovic *et al.,* 2009). Soil particle size distribution was done using Hydrometer method and soil carbonate was determined by the concentrated HCl acid method (Udovic *et al.,* 2009).

Tessier *et al.* (1979) total metal analysis method was used in the extraction of heavy metals from soil. Extraction was done by digesting 1 g (<0.005 mm) of soil sample with a mixture of 10 mL HF and 2 mL $HClO_4$ to near dryness; a second addition of 10 mL HF and 1 mL $HClO_4$ was made and again the mixture was evaporated to near dryness. Finally 1 mL $HClO_4$ 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. Atomic Absorption Spectrophotometer (AAS) model 210VGP, Buck Scientific Incorporated USA with air-acetylene flame was used for the determination of heavy metals in this work. Assessment of accuracy and precision was done through using three replicate samples, precision, spiking and 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 and Discussion

The physico-chemical properties of the studied soil are shown in Table 1 while Table 2 shows the concentration of heavy metals in dry and rainy season soil. Table 3 indicates Pearson correlations analysis for the studied metals. Analysis of soil Reference Material 989 from Netherland gave Cu 144.5±11.6 and Pb 253.8±13.8 μg/g against the standard values of 153±3.9 and 282±3.6 μg/g for Cu and Pb, respectively. Total soil concentration of Cd ranged from 0.12-0.18, Cu 0.08-0.18, Mg 0.04-0.04, Ni 0.05-0.17, Pb, 0.05-0.07 and Zn 0.03-0.04 μg/g. The metallic levels in the mining site and control sites were generally low. The mining site soil is mainly sandy, neutral, moderately high in carbonate and low in organic matter. Cd level during the RS was observed to be highest metallic level in all the studied metals followed by Cu during the DS. Zn and Pb levels were relatively low (Zn 0.03-0.04 and Pb 0.05-0.07 μg/g). Total soil metal level for Mg was same for both seasons. Total metal levels in the control farm were relatively lower than mining environment soil. The metallic levels observed were lower than the normal soil content intervals and maximum allowable limits of heavy metals in soils (Pendias and Dubka, 1992; Bero and Reaves, 1984).

Soil contains various functional groups which are effective agents for heavy metal sorption with soil properties such as the level of Fe, Al, and Mn oxides, hydroxides, clay content, texture and organic matter acting as controlling factors (Amen and Akpan, 2011; Hesterberg, 1998). Soil matrix constituting elements required for plant growth and those potentially toxic are important (Hesterberg, 1998). Their interaction affects the properties and processes in the soil which are determined by rainfall distribution, erosion and soil properties (pH, soil drainage, redox potential, organic matter and clay content) with the dominant process at any specific time determining the retention capacity of heavy metals. (Lee *et al.,* 2001; Hesterberg, 1998).

All the studied metals were present in the mining site soil which indicates that there are variations of metals in the topsoil of the mining site. Such variations could be due to aerial deposition from mining. According to Ullrich *et al.* (1999) such variation of metals in the topsoil could be attributed to historical mining and smelting. Generally the metal levels were low in both sites with metallic levels of mining site soil slightly higher than that of the control soil in both seasons. The lower concentration levels recorded on the control soil could be due to lower intensive activities, which induce the pollution of heavy metals.

The heavy metals present in the tailings, parent materials and agrochemicals provide the source for the degree of contamination observed in the mining site soil. There are reports that, in mining environments dust laden metals spread as a layer of dust on every surface in the area due to blasting of the rocks during mining (Jung, 2008; Jian-Min *et al.,* 2007; Zhou *et al.,* 2007).

Table 1. Physico-chemical properties of the studied soils

Parameter (%)	Mining site	Control
Sand	72.24	78.24
Silt	7.28	7.28
CO_3^{2-}	4.61	4.72
Clay	20.48	14.48
Tom	2.17	3.17
pH	7.3	8.3

Table 2. Concentration of heavy metals in dry and rainy season soils ± SD (µg/g)

Metal	Dry season	Rainy season	Mean conc.	Control
Cd	0.14 ± 0.01	0.18±0.02	0.16±0.02	0.10±0.01
	(0.17-0.18)[a]	(0.12-0.15)[a]	(0.14-0.18)[a]	(0.09-0.11)[a]
Cu	0.16±0.03	0.13±0.03	0.15±0.03	0.07±0.01
	(0.08-0.18)[a]	(0.14-0.17)[a]	(0.12-0.18)[a]	(0.06-0.08)[a]
Mg	0.04±0.002	0.04±0.002	0.04±0.02	0.03±0.003
	(0.04-0.04)[a]	(0.04-0.04)[a]	(0.01-0.05)[a]	(0.027-0.033)[a]
Ni	0.07±0.01	0.15±0.03	0.11±0.02	0.01±0.01
	(0.05-0.09)[a]	(0.13-0.17)[a]	(0.08-0.12)[a]	(0.00-0.02)[a]
Pb	0.06±0.02	0.07±0.004	0.07±0.01	0.02±0.001
	(0.05-0.07)[a]	(0.06-0.07)[a]	(0.06-0.08)[a]	(0.017-0.021)[a]
Zn	0.04±0.05	0.04±0.03	0.04±0.03	0.03±0.01
	(0.03-0.04)[a]	(0.03-0.04)[a]	(0.00-0.08)[a]	(0.02-04)[a]

a = range.

Table 3. Pearson correlations for the studied metals

Metals	Cd	Cu	Mg	Ni	Pb	Zn
Cd	1	-	-	-	-	-
Cu	1.000	1	-	-	-	-
Mg	-1.000	-1.000	1	-	-	-
Ni	0.916	0.920	-0.914	1	-	-
Pb	-0.309	-0.319	0.303	-0.664	1	-
Zn	0.838	0.844	-0.834	0.986	-0.778	1

Zhou *et al.* (2007) reported, that tailings as contributing 567, 1140, 2.48 and 191 µg/g of Cu, Zn, Cd and Pb, respectively to the soil around the Dabaoshan Mine in China. Weathering also leads to oxidation of sulphide bearing minerals which causes acid mine drainage (AMD) characterized by release of metals leading to high concentration of heavy metals, acidity and salinity of soil in agricultural lands in mining sites (Jian-Min *et al.,* 2007; Lin *et al.,* 2005).

Mining activities have various impacts such as oxidation of metal sulphides induces soil acidification and imped natural colonization of vegetation causing soil erosion (Jian-Min *et al.,* 2007; Lin *et al.,* 2005) and heavy metals, derived from mining activities, may be carried on to agricultural land by erosion. Thus the variations in metallic level observed during the RS could be due to erosion which results in uneven distribution of metals in certain part of the soil due to the topography of the land. Such reports have been given by earlier authors (Cebula and Ciba, 2005; Lin *et al.*, 2005; Lee *et al,*. 2001, Hesterberg, 1998), Cebula and Ciba (2005) reported very high levels of Pb (10 915 mg/kg), Cd (6.2 mg/kg) and Zn (1650 mg/kg) after erosion. This results in uneven distribution of heavy metals on the same plot i.e. above permissible levels and within permissible levels which made the area to be excluded from farmland.

The percentage of organic matter in the mining soil was relatively lower than the control site. The low metallic levels in the mining site topsoil could be due to low percentage of organic matter which indicates lower retention of metals than in the control soil. This explains the nearness observed in metallic level of the mining site soil to the control soil. Such effects have been reported previously by Jung (2008). Organic matter plays an important role in soil structure, water retention, cation exchange and in the formation of complexes (Yahaya *et al.,* 2009; Okoronkwo *et al.,* 2006). The organic matter content in soil for example makes metal such as Cu to be bound and made unavailable through formation of complexes. (Li *et al.,* 2005). The Cu is an essential micronutrient for physiological processes in plants such as photosynthesis and respiration, carbohydrate distribution, nitrogen and cell wall metabolism, seed production and disease resistance (Lin *et al.,* 2005). According to Clemente *et al.* (2008), organic matter level influences migration of metals to deeper soil fractions and causes difficulty in the dissolution of metals during extraction. Such soils have been reported to have low sorption capacity for metal ions (Jung, 2008). The percentage clay fraction in the mining site soil is observed to be low. Soils with high percentage sand and low percentage clay content have high pollutant leaching potentials which makes such soil risky to underground water (Okoronkwo *et al.,* 2006).

The mining site soil pH was observed to be neutral while the control site was alkaline. Cd adsorption to soil particles is reported to be greater in alkaline or neutral soils than acidic soil (Jung, 2008; Lisbeth *et al.,* 2008; Ullrich *et al.,* 1999). Soil pH is especially important in soil processes, such as determining the availability and solubility of heavy metals in soil and their transportation (Lisbeth *et al.,* 2008; Ullrich *et al.,* 1999; Hesterberg, 1998). At low pH, metals are more soluble in the soil solution thus increasing soil metal toxicity and uptake by plants (Yahaya *et al.,* 2009). Other soil properties could influence such effects. Lisbeth *et al.* (2008) reported that 10% Pb desorption was observed at pH 2.5 in a particular soil, whereas in another soil 60 % Pb was desorbed at the same pH. The mining site soil was observed to be moderately high in carbonate. According to Michaud *et al.* (2007), metals antagonize themselves in calcareous soils and plant Cu phytotoxicity in is reported to be greater in calcareous soils than non-calcareous soils. Calcareous and non-calcareous soils have been reported to occur within fields and this result in possible occurrence of toxicity in some parts of the soil and non toxic situation in another part within the same vicinity (Michanud *et al.,* 2007). When such situation exists in agricultural soils it is important to identify them and target strategies of managing such soils. The presence of sulphur in the mining site soil could cause the introduction of acid mine drainage most often associated with mines and waste left untreated (Zhou *et al.,* 2007). Acid mine drainage could cause removal of vegetation in the mine site resulting in soil erosion and pollution of the soil with heavy metals (Lin *et al.,* 2005). Elevated levels of Cd, Cu, Pb and Zn were found in plants grown on tailings of a Korean mine (Lee *et al.,* 2001).

There was no specific variation pattern between the rainy and dry season metal levels. This is in agreement with Jung and Thornton (1997) findings but disagrees with Yahaya *et al.,* (2009) and Lee *et al.* (2001), who reported higher levels during the DS. However, there were variations which could be due to changes in physico-chemical properties of soils during both seasons. Possible reason in the mining site could be related to distance from the mine, topographic features and wind dispersal patterns of metals. Such finding has been reported by previous authors. (Jung, 2008; Lin *et al.,* 2005; Lee *et al.,* 2001; Ullrich, 1999) According to Jung (2008) variations in metallic levels could be due to differences in soil mineralogy and origin. Lee *et al.* (2001) reported variation in metallic levels to be due to the precipitation of hydride, carbonate, sulfide and iron compounds. Other possible causes, such as non-equilibrium distribution of water, microbial mediated processes and variation in soil properties within a short distance due to changes in metal solubility have been reported (Hesterberg, 1998). However, anomalies in metallic levels could occur as a result of heavy metal deposition on soil surface from various sources such as emissions of metal-carrying dusts, gases and smoke from industrial undertakings or land filled industrial waste through atmospheric transportation (Galiulin *et al.,* 2002; Wong *et al.,* 2002).

Other researchers have reported variations during the RS to be due to the differences in the individual metal solubilities and dissolution of carbonates and oxides by acidic rain (Jung, 2008; Cebula and Ciba, 2005; Ukpebor and Unuigbe, 2003; Wong *et al.,* 2002).

The ANOVA analysis showed that the concentrations of individual heavy metals in the mining site soil were significantly higher ($p<0.05$) than the control soils, indicating that the mining site soil increased the heavymetal concentrations in soils.

These metallic levels are lower than that reported by Ezeh and Chukwu (2011) and Iorfa *et al.,* (2011) and within the range reported by Aremua *et al.* (2010) in mining environments in Nigeria. In furtherance the observed metallic levels were lower than the range reported in mining environment by Wu *et al.* (2010) in China, Ullrich *et al.* (1999) in Poland, Gutiérrez-Ginés *et al.* (2010) in Spain and Prathumratana *et al.* (2008) in Europe.

Pearson correlations for the studied metals (Table 3) show that the metals were closely correlated Cd/Cd, Cu/Cd, Mg/Cd, Ni/Cd, Zn/Cd, Cu/Cu, Cu/Mg, Cu/Ni, Cu/Zn, Mg/Mg, Mg/Ni, Mg/Zn, Ni/Zn, Zn/Zn except for Pb which correlated with only Ni. This shows that the studied metals except Pb are from the same origin. The presence of Pb in the soil can be attributed to the fuel used in the various machinery for the mining process. Such has been reported by previous authors (Stephanic, 1998). There was no significance at the 0.05 level and at the 0.01 level.

Conclusion

The exploitation of an iron ore mine in Itakpe, Nigeria, has made the soil metal polluted. Correlations studies show the studied metals except Pb to be closely correlated indicating that they are from the same origin. The results show that the soil is slightly polluted and with gradual buildup could become highly polluted. There is need for regular monitoring to target strategies for quality soil management.

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