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# Heavy metal accumulation in crop plants around Itakpe Iron Mine, Okene, Nigeria

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Heavy metal accumulation in plants is of importance due to toxicity effects in humans and other biota. Crop plants were sampled around Itakpe mine, Okene, Nigeria for the determination of the heavy metals cadmium (Cd), copper (Cu), magnesium (Mg), nickel (Ni), lead (Pb) and zinc (Zn) using Flame Atomic Absorption Spectroscopy. Crop plants samples were collected during the dry and rainy seasons and digested with 4:1 mixture of HNO<sub>3</sub> and HCIO<sub>4</sub>. Recovery studies gave 80-120 % for crop plants. The average mean concentration of metallic levels in crop plants were 0.07±0.01, 0.14±0.10, 0.02±0.01, 0.09±0.01, 0.06±0.02, 0.25±0.13  $\mu$ g/g. The heavy metal concentrations of crops grown on control soil were relatively lower than those in the Itakpe mining site soil. The observed concentrations of heavy metals in the studied plants were below the FAO/WHO limit guideline for food. The presence of Zn and Cu in plants and the higher level of metals observed in the mining site farm crops compared with the control farm show that agrochemicals and mining contribute to the metallic levels in the Itakpe mining environment.

Keywords: Crop plants, Heavy metal, Agrochemicals, Mining.

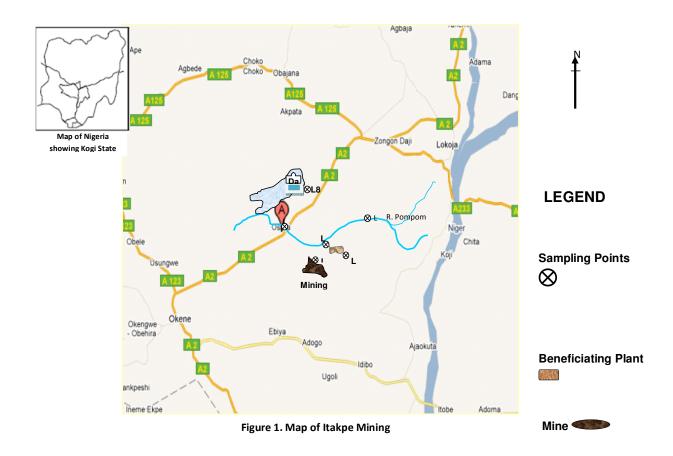
### INTRODUCTION

Pollutants are substances impairing the welfare of the environment through their activities in the various ecosystems. These contaminants are metals, agrochemicals, halogenated polycyclic hydrocarbons, food additives, dead organisms, sewage wastes and so on (Bridge, 2004; Duruibe et al., 2007; Wong et al., 2002). Metal depositions are associated with a wide range of sources such as industries (including battery production, mining, metal products, metal smelting and Cable coating industries); brick kilns; vehicular emissions; re-suspended road dust and diesel generator sets and so on (Bridge, 2004; Duruibe et al., 2007; Wong et al., 2002).

Mining processes lead to metal being released from their stable form into the environment and removal of large quantities of overburden waste materials. 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 (Arogunjo, 2007, Jian-Min et al., 2007). Thus agricultural lands can be contaminated. Soil is the fundamental material for food production and the loss of its fertile top which contains nutrients meant for plant survival results in poor productivity. This results in farmers resorting to use of various forms of soil amendments. Droughts and the need for increased food production all year round in developing countries have led to the use of irrigation in farming. The use of polluted water in irrigation results in various effects on soil (Rattan et al., 2005). According to Rattan et al., 2005, the irrigation of soil with sewage effluents caused 41% increase in organic matter content, 0.4 units drop in pH, significant build-up of extractable Zn, Cu, Fe, Ni and Pb to 208, 170, 170, 63 and 29% respectively and depletion of Mn by 31% in agricultural soil.

Continuous use of these supplements for soil amendment can potentially exacerbate the accumulation of metals in agricultural soils over time resulting in the

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deprivation of soil nutrients needed by plants to thrive (Arogunio, 2007; Ukpebor and Unuigbe, 2003). High concentration of metals in the soil cause risk to ecosystems (Arogunjo, 2007). The consequence is that crops grown on metal contaminated soils accumulate varying concentration of these metals, aquatic foods from polluted waters have high level of metals, meat and dairy products from livestock grazing on polluted pasture and drinking polluted water are polluted with metals (Arogunjo, 2007; Richtera et al., 2004 Lin et al., 2005, Pasquini, 2006). Heavy metals are one of a range of important types of contaminants that can be found in food crops. Pasquini, 2006 in the determination of metals in vegetables reported levels of metals 20 to 40 times higher than the WHO/FAO maximum recommended level. Sinha et al., 2010 reported the accumulation of Cr on the seeds of a plant to a level of 3.15 mg in a Cr contaminated soil. Some of the metals present in plant tissue are however essential metals which are required by plants in different concentrations for growth and development though their elevated levels can lead to enhancement in crop causing negative effects in plants and sometimes leading to plant death (Arogunjo, 2007; Wong et al., 2002; Sinha et al., 2010). Mg for example is the central atom of the chlorophyll molecule, and a requirement for plant photosynthesis. Cu is an essential micronutrient for physiological processes in plants such as photosynthesis, respiration, carbohydrate distribution, nitrogen and cell wall metabolism, seed production including also disease resistance and Zn is an essential trace metal required by plants for growth (Duruibe et al., 2007, Wong et al., 2002). These heavy metals are eventually passed into the human food chain. (Arogunjo, 2007).

The presence of metals in the food chain, leads to the local populace being exposed to multiple hazardous pollution sources which are potential threats (Bridge, 2004) Prolonged human consumption of unsafe concentrations of heavy metals in foodstuffs may lead to the disruption of numerous biological and biochemical processes in the human body. According to Marshall et al., 2003 heavy metal accumulation results in toxic concentrations in the body, with some elements acting as carcinogens and others associated with developmental abnormalities in children.

There is a growing global concern over the detection of metal in crops which affect food quality and safety. Food safety is a basic need for any population and supplying it is one of the World's most complex challenges especially in the face of an expanding population and environmental constraints (Arogunjo, 2007; Wong et al., 2002; Mashall et al., 2003). Plant crops are often grown in polluted and degraded environmental conditions.

As a result of mining dust from the tailings, mine waste dump and plant spillages constitute source of

contamination to the Itakpe mining environment. Local residents farm in the vicinity of the mine and there are reports on the use of various soil amendments to improve agricultural products. There is therefore cause for concern regarding contamination of food crops consumed by residents. The aim of the study is to determine levels of some heavy metals in some edible food crops grown around the Itakpe Iron mine in Kogi state, Nigeria and compare result with control site samples to access contamination level.

## Experimental

All reagents used were analytical grade (BDH, Poole, England). All glassware were washed with detergent, rinsed with distilled water, soaked in 10% HNO<sub>3</sub> for 24 hours and rinsed.

A total of 60 crop plant samples-maize (zea mays), (manihot esculentus), yam cassava (Dioscorea rotundata) and okro (Abelmoschus esculentus) were randomly collected in the vicinity of farms in the Itakpe mining site during the dry season (DS) in January and rainy season (RS) in July 2010. Control plant samples were collected from Osara Dam Area-12 kilometers from Itakpe. Figure 1 shows map of Itakpe with sampling points. The crop plant samples of species of interest were, washed with deionized water, air dried and dried to constant weight at about 105°C in an oven. Samples were ground into powder, passed through a 0.02 mm sieve, mixed to homogenize and stored in acid treated polythene bags. Method of 4:1 mixture of HNO<sub>3</sub> and HClO<sub>4</sub> by Kakulu and Jacob (2006) was used for plant digestion. The ground sample was redried at about 105°C for about 2 hours in the oven before each weighing and mixed to homogenize. 50 ml of 4:1 mixture of HNO<sub>3</sub> and HClO<sub>4</sub> was added into 1 g of sample and left to predigest for 24 hours. The sample was heated on a hot plate at about 100°C in a fume cupboard until the sample appeared a pale yellow or water white. The sample was transferred into 50 ml volumetric flask and diluted with de-ionized water to mark and filtered into clean plastic sample bottle ready for AAS analysis.

Reagent blank was prepared in similar manner. Spiking of the sample was done using standards of concentration of each studied metal and blank samples were extracted as above.

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 and spiking.

### **RESULTS AND DISCUSSION**

Recovery studies gave 80-120 % for the crop plants.

Table 1 shows the concentration of heavy metals in food crops in the rainy season (RS) while Table 2 shows the concentration of heavy metals in food crop (cassava) in the dry season (DS). Generally the metal levels in the plants in both farms were low with the control farm lower than the mining site farm. Metal concentrations varied with each plant type. In addition there was no specific variation pattern between the rainy season metal levels and the dry season levels. Mean metal concentrations in cassava, maize, yam and okro of Cd ranged 0.01 to 0.14. Cu 0.01 to 0.22, Mg 0.01 to 0.03, Ni 0.05 to 0.15, Pb 0.05 to 0.07 and Zn 0.01-0.87 µg/g. Concentration of Cd in food crops showed maize leaves to have the highest level (0.14  $\mu$ g/g) followed by Yam (0.05  $\mu$ g/g), Cu showed okro leaves to have the highest level (0.22 µg/g) followed by cassava leaves (0.18 µg/g), Mg showed cassava leaves to have the highest level (0.03  $\mu$ g/g) followed by okro (0.02 µg/g), Ni showed maize leaves to have the highest level (0.15  $\mu$ g/g) followed by cassava (0.12  $\mu$ g/g). Pb showed the same level (0.05  $\mu$ g/g) in all the food crops while Zn concentration in food crops showed yam leaves to have the highest level (0.87  $\mu$ g/g) followed by cassava (0.48 µg/g) in the control farm. Except for Zn the metallic levels of the studied metals were the same in the mining site farm and the control farm during the dry season. Cu and Ni levels were relatively higher than the other studied metals in all the food crops.

Climate is of great significance in every phase of agricultural activity. This has remained an uncontrolled factor in crop production except in cases of environmental modification or where there is wide variation in climate between seasons, which can cause seasonal variations in nutrient uptake (Lavanya et al., 2010). Some plants are reported to take up heavy metals through their roots along with nutrients intake while others take up metals through foliar adsorption (Khan et al., 2005; Hesterberg, 1998). There is report that at least 50% of Pb contamination is found on the surface of vegetables (Mashall et al., 2003). Metals such as Cd and Zn have been reported to be relatively mobile within plants (Olalade and Ologundudu, 2007; Dahmani-Muller et al., 2002). Report is given of the translocation of Cd and Zn within plants been greater than that of Cu and Pb indicating that different plants have different rate of metal transport within plants (Dahmani-Muller et al., 2002; Jung, 1997).

The metallic levels of metals in the mining site farm were slightly higher than the control farm crops. These levels are lower than that reported in crop plants by Jung and Thornton (1996) in the vicinity of Lead-Zinc mine, Korea, Jung (2008) in the vicinity of a Korean Cu-W mine and that reported by Lee et al., (2001) in the vicinity of the Daduk Au-Ag-Pb-Zn mine in Korea. Factors influencing the bioavailability of heavy metals in plants are reported to be soil pH, organic matter, cation exchange capacity, moisture, presence of microorganisms, plant species, plant age, soil texture,

	Cassava	Maize	Yam	Okro
Cd				
Mining site	0.01±0.01	0.01±0.002	0.03±0.01	0.03±0.002
•	(0.00-0.02) <sup>a</sup>	(0.008-0.012) <sup>a</sup>	(0.02-0.04) <sup>a</sup>	(0.018-0.032) <sup>a</sup>
Control	0.02±0.01	0.14±0.01	0.05±0.004	· · · · ·
	(0.01-0.03)	(0.13-0.15) <sup>a</sup>	(0.046-0.054) <sup>a</sup>	
Cu	· · · · · ·		· · · ·	
Mining site	0.18±0.16	0.09±0.002	0.15±0.01	0.22±0.03
3	(0.02-0.34) <sup>a</sup>	(0.088-0.092) <sup>a</sup>	(0.14-0.0.16) <sup>a</sup>	(0.019-0.25) <sup>a</sup>
Control	0.11±0.01	0.08±0.01	0.14±0.01	(0.0.0.0.0.0.0)
	(0.10-0.12) <sup>a</sup>	(0.07-0.09) <sup>a</sup>	(0.13-0.15) <sup>a</sup>	
Ma	(0	(0.00 0.00)	(0110 0110)	
Mining Site	0.03±0.001	0.01±0.01	0.01±0.002	0.02±0.01
	(0.029-0.031) <sup>a</sup>	$(0.00-0.02)^{a}$	(0.008-0.012) <sup>a</sup>	(0.01-0.03) <sup>a</sup>
Control	0.02±0.002	0.02±0.004	0.03±0.001	(0.00 0.000)
	(0.018-0.022) <sup>a</sup>	(0.016-0.024) <sup>a</sup>	(0.027-0.031) <sup>a</sup>	
Ni	()	(/	()	
Mining site	0.12±0.01	0.15±0.01	0.11±0.01	0.09±0.01
3	(0.11-0.13) <sup>a</sup>	(0.14-0.16) <sup>a</sup>	(0.10-0.12) <sup>a</sup>	(0.08-0.10) <sup>a</sup>
Control	0.06±0.01	0.05±0.001	0.08±0.01	()
	(0.05-0.07) <sup>a</sup>	(0.049-0.051) <sup>a</sup>	(0.07-0.09) <sup>a</sup>	
Pb	(0.00 0.00)	(	(0.00 0.00)	
Mining Site	0.05±0.001	0.05±0.02	0.05±0.02	0.05±0.01
	(0.049-0.051) <sup>a</sup>	(0.03-0.07) <sup>a</sup>	(0.03-0.07) <sup>a</sup>	(0.04-0.06) <sup>a</sup>
Control	0.07±0.02	0.06±0.02	0.06±0.01	(0.0.0.000)
	(0.05-0.09 <sup>a</sup>	(0.04-0.08) <sup>a</sup>	(0.05-0.07) <sup>a</sup>	
Zn	(0.00 0.00	(0.0.000)	(0.00 0.01)	
Mining Site	0.02±0.01	0.02±0.004	0.03±0.01	0.05±0.01
	(0.01-0.03) <sup>a</sup>	(0.016-0.024) <sup>a</sup>	(0.02-0.04) <sup>a</sup>	$(0.04-0.06)^{a}$
Control	0.48±0.14	0.01±0.01	0.87±0.57	(0.01 0.00)
0011101	$(0.34-0.64)^{a}$	(0.00-0.02) <sup>a</sup>	(0.30-1.44) <sup>a</sup>	

Table 1. Concentration of heavy metals in food crops in the rainy season (µg/g dry weight)

a= range

Table 2.	Concentration	of	heavy	metals	in	food	crops
(cassava) in the dry Season (μg/g dry weight)							

Metal	Mining site farm	Control
Cd	0.03±0.002	0.03±0.002
	(0.028-0.032) <sup>a</sup>	(0.028-0.032) <sup>a</sup>
Cu	0.01±0.002	0.01±0.002
	(0.018-0.012) <sup>a</sup>	(0.018-0.012) <sup>a</sup>
Mg	0.1±0.02	0.1±0.01
	(0.08-0.12) <sup>a</sup>	(0.09-0.11) <sup>a</sup>
Ni	0.01±0.004	0.01±0.004
	(0.006-0.014) <sup>a</sup>	(0.006-0.014) <sup>a</sup>
Pb	0.01±0.002	0.01±0.003
	(0.008-0.012) <sup>a</sup>	(0.007-0.013) <sup>a</sup>
Zn	0.04±0.01	0.02±0.01
	(0.03-0.05) <sup>a</sup>	(0.01-0.03) <sup>a</sup>

a= range

time interval of metallic soil input, topography, nutrient availability and interaction among the metals with total metal concentrations in soils and soil pH controlling their intake (Lee et al., 2001; El-Sharkawy, 2008; Codex Alimentarius Commission, 2001).

There was no specific pattern for the distribution of

metals in both farms. However there is possibility of anomalies in metallic levels due to heavy metal deposition on soil and foliar surface from various sources such as emissions of metal-carrying dusts, gases and smoke from industrial undertakings or use of agrochemicals. For example high Zn concentration was observed at the control farm in cassava and yam crops. This could be due to direct deposition on plant leaves through the use of agrochemicals. Such has previously been reported (Bridge, 2004; Jian-Min et al., 2007; Jung and Thornton, 1996).

There were no specific patterns in seasonal variations in the metallic levels in the different crops but however there were variations in metallic content of different plant species growing on the same soil. Variations in metal content of plants could be due to seasonal changes which modifies bioavailability with pattern varying with each metal (Wong et al., 2002; Pasquini, 200; Kakulu and Jacob, 2006). This disagrees with Lee et al., (2001) and Jung and Thornton (1996) who reported higher metallic levels during the dry season. Low metallic level during the rainy season is reported to be due to the precipitation of hydride, carbonate, sulphide and iron compounds (Lee et al., 2001). Effects such as decrease in soil pH for example is reported to result in an increase in heavy metal absorption by plants due to dissolution of metalcarbonate complexes releasing metals into solution during the rainy season (Mapanda et al., 2004). Other possible reasons for metal level variation in plant crops during rainy season could be due to the differences in soil properties, uneven distribution of metals in soil, variation in heavy metal contamination level of the soil and continuous atmospheric deposition of these metals which could increase their level in the soil even after some have being absorbed by the plants (Hesterberg, 1998; Hosseinpur and Dandanmozd, 2010).

ANOVA analyses on the crops in all the farms shows that there were significant differences (p<0.05) shown in Cu, Zn and Ni in the crops during the rainy season. The significant difference (p<0.05) could be due to the high concentration of these metals in the soil. According to Lee et al., (2001) metal concentration in plants increase with those in soil. Other authors have also reported correlation between Cu in soil and plant uptake Lestan et al., 2003). This disagrees with Pasquini (2006) who reported no correlations between plants and soil concentration levels of Fe, Mn, Cu, Zn, Ni and Pb. In furtherance the significant level of Cu and Zn could be as a result of their need by plants as essential elements and their being components of pesticides (Borah and Devi, 2010; Sharma, 2010). Use of copper oxychloride pesticide has been reported to increase Cu concentration in soil and consequently in edible crops. (Modaihsh et al., 2004). Pesticides and fungicides have also been reported to have components such as As, Hg, Cu, Zn and Pb (Modaihsh et al., 2004). The significant difference (p<0.05) observed in Ni in all the farms could be attributed to the presence of high level of Ni in the atmosphere (Galiulin et al., 2002).

Some researchers have reported low metal levels during the rainy season as a result of erosion effect that is capable of removing heavy metals from the soil thereby diluting the soil solution (Pasquini, 2006); El-Sharkawy, 2008).

Apart from cassava plant other crop plants were not available during the dry season. In all the cassava plants the concentrations of heavy metals during the dry season were of the same concentration level (0.03 µg/g) except for Zn where there were small variations indicating same plant species in different locations absorb heavy metal equally when soil properties are similar. The no significant difference (p>0.05) observed in cassava crop in some of the metals during the dry season could be as a result of the cassava leaf characteristic. Cassava leaf is reported to have high photosynthetic capacity and high stomata sensitivity to air humidity which reduces water losses during the dry season when plants are subjected to decrease in soil water as well as to high atmospheric evaporative demands, thus protecting leaves from severe dehydration (Hesterberg, 1998; El-Sharkawy, 2008). This can result in high level of metal concentration and such reports have been given in previous studies (Hesterberg, 1998; El-Sharkawy, 2008).

Previous research reported high metallic levels during the dry season to be due to possibility of atmospheric deposition of heavy metals on plant leaves, evaporation process removing water from soil, causing increase in metal concentration in the roots and leaves and possibility of use of contaminated water for irrigation (Jung, 1997; Lee et al., 2001).

Comparison of heavy metal concentration in the studied crops with those grown on control farm show relatively lower metal concentration of Cd, Cu, Mg, Ni, Pb and Zn. The observed metallic levels where below the FAO/WHO limit guideline values for heavy metal levels in food (Codex Alimentarius Commission, 2001)

### CONCLUSION

The heavy metal concentrations of crops grown on control soil were relatively lower than those in the ltakpe mining site soil. The observed concentrations of heavy metals in the studied plants were below the FAO/WHO limit guideline for food. The presence of Zn and Cu in plants and the higher level of metals observed in the mining site farm crops compared with the control farm show that agrochemicals and mining contribute to the metallic levels in the Itakpe mining environment. Regular monitoring of metals in plants is essential for prevention of excessive buildup of the metals in the food chain.

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