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A physico-chemical analysis of soil and selected fruits in one rehabilitated mined out site in the Sierra Rutile environs for the presence of heavy metals: Lead, Copper, Zinc, Chromium and Arsenic

P. O. Egbenda*, F. Thullah and I. Kamara

Department of Chemistry, Fourah Bay College, University of Sierra Leone, Freetown, Sierra Leone.

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The accumulation of heavy metals in soils especially in mining environments is of increasing concern to researchers in the Agricultural Industry. This is because the metals are biomagnified by plants. Accumulation of heavy and trace metals in plants occur by various sources but soil is considered the major one. Consumption of vegetables and fruits containing heavy metals is one of the main ways in which these elements enter the human body. Once in the body, heavy metals are deposited in bone and fat tissues, overlapping noble minerals and cause an array of diseases. The present study investigated the concentration of heavy metals that is, Cu, Zn, Cr, As and Pb in soil as well as mango (*Mangifera indica* L.) and cashew (*Anacardium occidentale*) fruit samples collected from the Mokaba rehabilitated site in the Sierra Rutile environs, to evaluate the possible health risks to human body through food chain transfer. Atomic absorption spectrophotometry was used to estimate the levels of these metals in the fruits and soil. Results showed that the concentrations of Pb and Cu in both soil and fruits are higher than the World health average values. However, Zn and Cr were found to be below the World health average values, whereas As was not detected. Translocation factors (TF) from soil to fruits were calculated from the data on levels of metals in both soil and fruits. The sampled plants showed high translocation factor values (TF > 1in almost all cases) implying that the plants could be labeled as accumulators of pollution. Pearson's product moment correlation showed a very strong relationship between soil and fruits. It can be concluded that the crops/plants grown in the rehabilitated lands in the Sierra Rutile environs absorb significant levels of some heavy metals from the polluted soil.

Key words: Rehabilitated, heavy metals, bioaccumulation, translocation, bioavailability, biomagnified.

INTRODUCTION

Heavy metals are significant environmental pollutants, and their toxicity is a problem of increasing concern for ecological, evolutionary, nutritional and environmental reasons. In addition to being non biodegradable, heavy

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*Corresponding author. E-mail: p_egbenda@yahoo.com

metals have long biological half-lives as well as the potential to accumulate in different body organs, leading to unwanted side effects. One consequence of mineral exploitations is the exposure of metals to the earth's surface. After several years of operation, the Sierra Rutile mining Company has left behind lakes, mine spoil heaps and sand tailings in many areas of land that were once viable for agricultural activities. The mine spoil heaps and sand tailings are believed to contain various heavy metals in different forms. In order to restore the mined out areas into productive agricultural resources, the Company established land and water rehabilitation programmes. The Mokaba rehabilitated land is one of the mined out sites that was rehabilitated several years before the civil war in Sierra Leone. The site is about half a mile from Mokaba town, a fairly large settlement in the Impere Chiefdom, in Bonthe District, in the Sierra Rutile environs. A variety of economic trees such as mango, guava, cashew, coconut and oil palm have been grown at the Mokaba site. Fruits from these plants are harvested and sold to communities in the Sierra Rutile environs. Notably fruits and vegetables are rich sources of vitamins, minerals and fibers. They also have beneficial anti-oxidative properties. Sadly however, plants can take up heavy metals from contaminated soils through root systems. Consumption of fruits and vegetables contaminated with heavy metals may pose a risk to human health (Sal Jasir et al., 2005). The aim of this study is to carry out a physicochemical analysis of soil and fruits (cashew, *Anacardium occidentale* and mango, *Mangifera indica* L.) from the Mokaba site to ascertain soil pollution and to provide guidance for pollution assessment and control in the rehabilitated lands in the Sierra Rutile environs.

Heavy metals in soil environment

Heavy metal contamination of soil results from anthropogenic processes such as mining, smelting procedures and agriculture as well as natural activities (Aziz et al., 2004). Heavy metals are generally present in agricultural soils at low levels. Due to their cumulative behaviour and toxicity, however, they have a potentially hazardous effect not only on crops but also on human health (Slagle et al., 2004). High concentration of heavy metals in soils is toxic for soil organisms such as bacteria, fungi and higher organisms (Elvingson and Agren, 2004). In soil Lead tightly binds itself to organic soil particles which may decrease its mobility and reduce uptake by plants (Cooper et al., 1999). It has been suggested that the mobility of lead and copper is greater in sandy soils, with apparently very little organic matter, than in organic soils. Chromium exists in two possible oxidation states in soils namely Cr(III) and Cr(VI). The Cr(VI) ions are more toxic than Cr(III) ions. Because of the anionic nature of Cr(VI), its association with soil surfaces is limited to positively charged exchange sites, the number of which decreases with increasing soil pH. Cr(VI) was found to be highly mobile in alkaline soils (Griffin and Shimp, 1978) and can be reduced to Cr(III) under normal soil pH and redox conditions. Soil organic matter has been identified as the electron donor in this reaction (Bartlett and Kimble, 1976). The presence of sulfate can enhance Cr(VI) adsorption to kaolinite (Zarchara et al., 1988). The parameters that correlated with Cr(VI) immobilization in the soils were free iron oxides, total manganese, and soil pH. On the other hand, soil properties, cation exchange capacity, surface area, and percent clay had no significant influence on Cr(VI) mobility (Rai et al., 1987). Zinc is readily adsorbed by clay minerals, carbonates, or hydrous oxides. The greatest percent of the total Zn in polluted soils and sediments is associated with Fe and Mn oxides. Zinc hydrolyses at pH>7.7 and the hydrolyzed species are strongly adsorbed to soil surfaces. It also forms complexes with inorganic and organic ligands that will affect its adsorption reactions with the soil surface (Hickey and Kittrick, 1984). Acidic and sandy soils with low organic content have a reduced capacity for zinc absorption. Copper may exist in soils in the following forms: water soluble, exchangeable, organically bound, associated with carbonates and hydrous oxides of Fe, Mn and Al, and residual. Copper is adsorbed on the soil, forming an association with organic matter, Fe and Mn oxides, soil minerals, etc., thus making it one of the least mobile of the trace metals (Ioannou et al., 2003). The metal is retained in soils through exchange and specific adsorption mechanisms. Clay mineral exchange phase may serve as a sink for Cu in noncalcareous soils. In calcareous soils, specific adsorption of Cu onto $CaCO_3$ surfaces may control Cu concentration in solution (Cavallaro and McBride, 1978). Arsenic exists as either arsenate, (AsO_4^{3-}), or arsenite, (AsO_3^{3-}) in the soil environment. Arsenite is the more toxic form of arsenic. Arsenite compounds are reported to be 4 to 10 times more soluble than arsenate compounds. In the adsorption by kaolinite and montmorillonite, maximum adsorption of As(V) occurs at pH 5. Adsorption of arsenate by aluminum and iron oxides is a maximum at pH 3 to 4 and gradually decrease with increasing pH (Anderson et al., 1976). As(III), is also strongly pH-dependent. It was observed that an increase in sorption of As(III) by kaolinite and montmorillonite occur over a pH range of 3 to 9 (Griffin and Shimp, 1978). The maximum adsorption of As(III) by iron oxide occurred at pH 7. Adsorption of As(III) is rapid and irreversible on some soils. Formation of As(III) also may lead to the volatilization of arsine (AsH_3) and methyl- arsines from soils (Woolson, 1977). The loss of organic arsenic compounds from the soil was far greater than for the inorganic source of arsenic. As(III), can be oxidized to As(V) in which manganese oxides act as primary electron acceptor (Oscarson et al., 1983).

Uptake and translocation of heavy metals in fruits

Migration of metals in the soil is influenced by physical and chemical characteristics of each specific metal and by several environmental factors; the most significant appear to be: soil type, total organic content, redox potential, and pH (Murray et al., 1999). The fate of heavy metals in polluted soils is a subject of study because of the direct potential toxicity to biota and the indirect threat to human health via the contamination of groundwater and accumulation in food crops (Martinez and Motto, 2000). Heavy metal pollution of soil enhances plant uptake causing accumulation in plant tissues and eventual phytotoxicity and change of plant community (Gimmler et al., 2002). Compounds accumulate in living organisms any time they are taken up faster than they are broken down (metabolized) or excreted (O'Brien, 2008).The soil to plant transfer factor known as Translocation Factor (TF) is one of the important parameters used to estimate the possible accumulation of toxic elements, especially radionuclides through food ingestion (El-Ghawi et al., 2005). Translocation Factor (TF) is the transfer capability of heavy metals from soil to various parts of the plant. TF of heavy metals depends upon bioavailability of metals, which in turn depends upon its concentration in the soil, their chemical forms, difference in uptake capability and growth rate of different plant species (FAO/WHO, 2011). TF > 1, indicates that the plant translocate metals effectively from root to the shoot (Baker and Brooks, 1989). Most plants translocate inorganic and nutrient constituents from roots to leaves (Roselli et. al., 2003). Higher values of TF also suggest poor retention of metals in soil and/or more translocation in plants (indicating stronger accumulation of the respective metal by that fruit). The higher uptake of heavy metals in fruits may be due to higher transpiration rate to maintain the growth and moisture content of plants (Gildon and Tinker, 1981). A related study reported highest translocation factor for heavy metals through leafy vegetables. The TF does not present the risk associated with the metal in any form. The degree of toxicity of heavy metal to human beings depends upon their daily intake (Sridhara et al., 2008). Several studies have indicated that crops grown on soils contaminated with heavy metals have higher concentrations of heavy metals than those grown on uncontaminated soil (Nabulo, 2006). The translocation factor (TF) of heavy metals can be calculated as follows:

$$\text{TF} = \frac{\text{Metal concentration in fruit (shoot)}}{\text{Metal concentration in soil in which fruit was grown (root)}}$$

MATERIALS AND METHODS

Sampling

Soil samples were collected from the Mokaba site at different locations (A, B, C, D and E) and at variable depths ranging from 0 to 10 cm from the surface. Fresh ripe cashew fruits (*A. occidentale*) and mango fruits (*M. indica* L.) were collected from the trees at locations indicated in Figure 1 (not to scale).

Sample preparation

The soil samples were air–dried in an oven at 50°C temperature until constant weight. The cashew (*A. occidentale*) and mango (*M. indica* L.) fruits were washed thoroughly with distilled water, peeled, sliced and then dried in oven at 60°C. The dried fruit and soil samples were powdered in an agate mortar, homogenized and sieved in a 60 micron sieve. The powdered samples were stored in clean stoppered sterile bottles (Djingova et al., 1993; Keane et al., 2001).

Heavy metal analysis

Five grams of soil sample was placed in a 250 ml beaker followed by addition of 50 ml distilled water and 60 ml aqua regia (HNO_3: HCl;3:1). Boiling chips were added and the mixture digested on a hot plate at 100°C for one hour and at125°C for further 15 min to concentrate to 5 ml volume. The 5 ml volume concentrate wascooled, 1 ml 30% H_2O_2 added and then heated for further 10 min. The hot solution was again cooled and then treated with 3 ml 30% H_2O_2 before heating for another 10 min. 50 ml distilled water and 25 ml HCl was added to the solution and then heated to boiling. The resulting hot solution was cooled, filtered and then diluted to 250 ml with distilled water.

10 ml HNO_3 was added to 2 g of the powdered fruit sample in a 100 ml beaker and the mixture heated at 40°C for 15 min. To the cooled digest 5 ml concentrated HNO_3 was added and then heated for another 30 min at 40°C to concentrate to 5 ml volume. 5 ml H_2O was added to the solution followed by 3 ml 30% H_2O_2. The beaker was covered and the solution gently heated until vigorous effervescence occurred. 1 ml 30% H_2O_2 was added to the solution followed by gentle heating until effervescence subsided. 5 ml concentrated HCl was added followed by 10 ml distilled water and the resulting solution heated for 15 min, cooled, filtered using ash less filter paper and then diluted to 60 ml with distilled water.

The concentrations of Pb, Cr, Cu, Zn and As were determined in soil, cashew and mango fruit samples using the PG-800 Atomic Absorption Spectrophotometer. The working standards were prepared by diluting concentrated stock solution of 1000 mg/L for Cu, Cr and Zn and 1000 µg/L for As, and Pb in deionized water. The matrix modifiers $NH_3H_2PO_4$ and Mg $(NO_3)_2$ were used.

RESULTS AND DISCUSSION

The results for pH and conductivity measurements of the soil samples in five different locations are given in Table 1. The WHO and E.U recommended limits for pH and conductivity in soil are given in Table 2. The pH of the soil at the Mokaba site has a range of 4.90 to 5.24 and mean value of 5.11 (Table 1).This implies that the soil is acidic compared to the pH values of WHO (6-5) and EU (6-8). The pH has a great impact on bioavailability in the soil. At high pH metals tend to form insoluble metal mineral phosphates and carbonates, whereas at low pH they tend to be found as free ionic species or as soluble organometals and are more bio available (Sandrin and Hoffman, 2007; Twiss et al., 2001; Rensing and Maier,

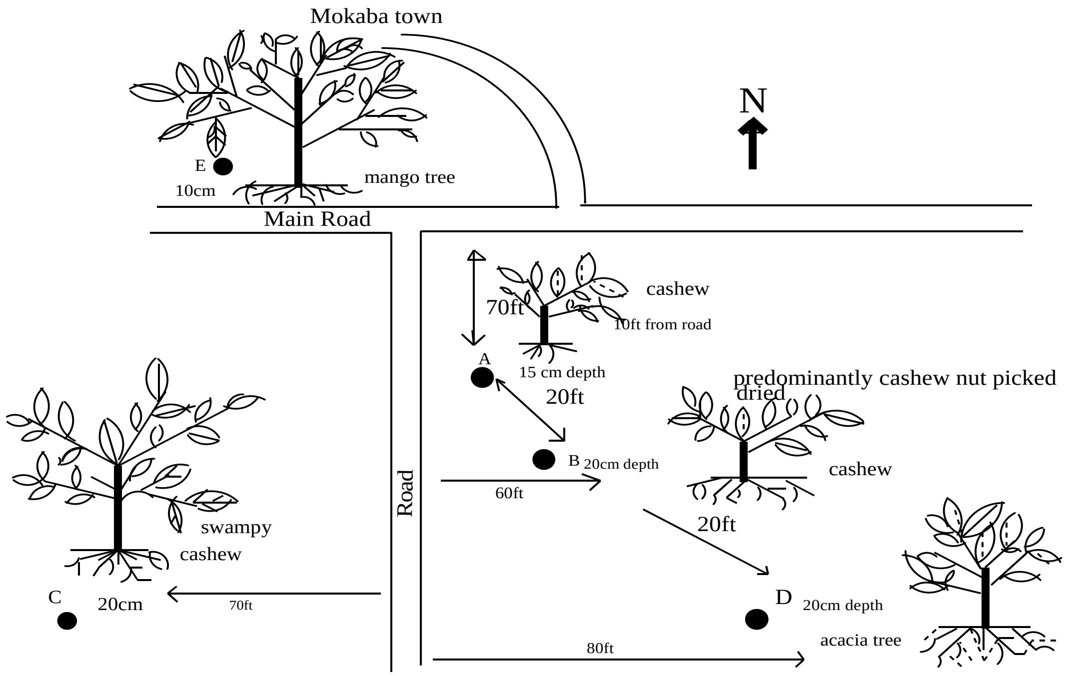

Figure 1. Sketched map of the samples collection sites.

Table 1. pH and conductivity in the soil.

Location	pH	Conductivity (S/cm)
A	4.90	0.02
B	5.24	0.01
C	5.12	0.01
D	5.14	0.01
E	5.15	0.01
Mean value	5.11	0.01

Table 2. Recommended values for pH and Conductivity by WHO and EU in soil.

Parameter	WHO	EU
pH	6-5	6-8
Conductivity (μS/cm)	250	250

2003; Naidu et al., 1997). The measured conductivity values of the soil samples (0.01-0.02 S/cm) testify the presence of trace metal ions or ionizable materials in the soil.

Table 3 gives the concentrations of the metals in the soil and fruit samples (in mg/L). The WHO recommended limits of the investigated metals Pb, Zn, Cr, Cu and Asin mg/L are given in Table 4. Both mango and cashew fruit samples showed higher average metal content for the elements Cu, Pb and Zn (Table 3) and relatively lower values for Cr. This is because Cr accumulates mainly in roots followed by stems and leaves and that only small amount of the metal is translocated to leaves (Tiwar et al., 2009; Huffmann and All away, 1973). Also the mango fruit tend to bio accumulate Pb, Zn and Cu more whereas cashew fruit tend to bio accumulate Zn and Cu more. The mango fruit bio accumulates Pb metal more than the cashew fruit whereas the cashew fruit bio accumulates

Table 3. Average concentrations of metals in soil and fruits (in mg/L).

Element	Soil (mg/L)	Mango (mg/L)	Cashew (mg/L)
Pb	0.053	0.355	0.055
Zn	0.222	0.396	0.685
Cr	0.027	0.019	0.025
Cu	0.817	0.847	1.140
As	ND	ND	ND

Table 4. WHO recommended permissible limits of the metals (Pb, Zn, Cr, Cu and As in mg/L in fruits.

Metal	Permissible limit
Pb	0.050
Zn	<5.000
Cr	<0.050
Cu	<1.000
As	0.010

Table 5. Translocation factors (TF) in mango and cashew fruit samples.

Metals	TF in mango fruit	TF in cashew fruit
Pb	6.698	1.038
Zn	1.784	3.086
Cr	0.704	0.926
Cu	1.037	1.395

Zn, Cu and Cr more than the mango fruit. Cu has the highest concentration in the soil (0.817 mg/L) and fruits (0.847 mg/L in mango and 1.140 mg/L in cashew). This could be due to the presence of different forms of copper in the soil e.g. water soluble, exchangeable, organically bound, associated with carbonates and hydrous oxides of Fe, Mn, Al, and residual (Ioannou et al., 2003). Moreover the levels of Zn and Cu were found to be higher in the cashew fruit (younger trees) than in the mango fruit (older trees). This suggests that younger plants bio accumulate heavy metals more than older ones. In both soil and fruits the average concentrations of heavy metals follow the order: Cu > Zn >Pb> Cr. Arsenic was not detected in any of the fruit samples.

Table 3 also shows concentration of metals to be higher in fruits than in the soil. This could be due to loss in soil by leaching and uptake by the plant growing there including the plants under investigation. The sampled plants showed high translocation factor values (TF > 1in almost all cases) implying that the plants could be labeled as accumulators of pollution (Table 5). Trends in translocation factor are: for Mango (*M. indica* L.), Pb>Zn>Cu>Cr, and for Cashew (*A. occidentale*), Zn > Cu > Pb > Cr. The high TF values could be attributed to low retention rate of the metals in the soil. Pearson's product moment correlation reveal a very strong correlation between soil and mango ($R_m^2 = 0.925$) and between soil and cashew ($R_c^2 = 0.933$) fruits. This implies that the source of the extra metal concentrated by the fruits is most likely the soil.

Conclusion

This study revealed that the soil in the rehabilitated Mokaba site carry significant levels of heavy metals. The buildup of heavy metals in soil profile may prove detrimental not only to plants and animals which bio accumulate them, but also to consumers of the harvested fruits from the farms. It is therefore suggested that other economic trees such as rubber (for rubber), acacia and eucalypti (for charcoal) be cultivated in the rehabilitated lands to reduce human health risk to metal pollution.

Conflict of Interest

The authors have not declared any conflict of interest.

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