African Journal of Biotechnology Vol. 9 (18), pp. 2675-2682, 3 May, 2010
Available online at http://www.academicjournals.org/AJB
ISSN 1684–5315 © 2010 Academic Journals

Full Length Research Paper

Preliminary investigation of chemical fractionation and heavy metal accumulation in plant maize (*Zea mays*) grown on chromated copper arsenate (CCA) contaminated soil amended with poultry droppings

E. U. Ikhuoria, S. O. P. Urunmatsoma* and F. E. Okieimen

Department of Chemistry, Geochemical Research Laboratory, University of Benin, Benin City, Nigeria.

Accepted 22 March, 2010

Poultry droppings used as soil amendments and a sequential chemical speciation (six steps) procedure were used to predict the uptake of Cr, Cu and As by maize (*Zea mays*) plant in chromated copper arsenate (CCA) contaminated soil. A pot experiment containing contaminated soil samples to different percentage levels of amendments and control (no amendment) was set up. The initial concentration of Cr, Cu and As in the contaminated soil sample were established. The six fractions based on sequential extractions were also established. The distribution patterns of the metals based on their mobility factor M_f showed values high enough to predict high lability and bioavailability for arsenic, moderate for chromium and low for copper. The amendment, an energy-rich source substance enhanced mobility and bioavailability of the metals and their subsequent uptake and accumulation in the maize plant. This led to a cleanup at 20% amendment of As (20.6%), Cr (2%), and Cu (17.1%) after a period of twenty days. These figures are impressive considering the fact that the increase in pH occasioned by the poultry dropping amendment must have bound the metals.

Key words: CCA contaminated soil, amendment, copper, maize (*Zea mays*).

INTRODUCTION

Man's environment is under constant threat from his own activities. Man's expanding population, industrialization; urbanization, intensive agriculture etc have caused tremendous damage to the environment. There has been increasing deposition of heavy metals on land in recent years (Khodadoust et al., 2005). This has given rise to considerable concern because of its toxicity, bio-accumulating tendency, threat to human life and the environment (Horsfall and Spiff, 2005; Faisal and Hasnain, 2004; Igwe and Abia, 2003; Qun et al., 2004), particularly as regards groundwater contamination (Alloway, 1995). This risk to human health is through a complex interconnected relationship known as food web. The exploitation of natural resources has further aggravated the problem. Preservation and proper management of the environment is lacking. The essential of ensuring sustained development of the society is non existence.

Heavy metals are among pollutants that are not subject to bacterial attack or other break down or degradation process and are permanent additions to water bodies (El-Nady and Atta, 1996). As a result of this, their concentrations often exceed the permissible levels normally found in soil, water bodies and sediments.

The rampant use of chemical fertilizers contributes largely to the deterioration of the environment through depletion of fossil fuels, generation of carbon dioxide (CO_2) and contamination of water resources. This loss of soil fertility due to imbalance use of fertilizers has adversely impacted agricultural productivity and causes soil degradation (Nagavallemma et al., 2004). Now there is a growing realization that the adoption of ecological and sustainable farming practices can only reverse this declining trend in the global productivity and environment protection (Wani et al., 1995).

---

*Corresponding author. E-mail: unnyrunmatsoma@yahoo.com. Tel: +234 803 441 2284.

In Nigeria, millions of tons of organic waste are generated annually. For a country that does not have a proper legitimated waste disposal system, these wastes pose a problem for safe disposal. Most of these wastes could be seen around abattoirs, poultry areas, in and around markets and a host of other places where a number of organisms (macro and micro) that have the ability in nature's laboratory do their work. Some of the product of their conversion is plant nutrient and organic matter.

In the face of these limitations and its associated dangers, far reaching measures were considered. Information about the desired limits of contaminants, monitorring, and control became necessary for pollution abatement. A number of national and international conferences were held to correct the mistakes of the past. One of such successful meetings was the 1992 Earth Summit at Rio de Janeiro in Brazil where more than 100 Heads of Government representing both developing and developed countries participated. The general consensus of the summit was that environment and development should not be treated as contrary but rather complementary to each other. Agenda 21 of the Summit provides a nonbinding action plan to meet the needs of global economic development with protection of the environment. Phytoremediation is a promising method for the cleaning of soil and water. It involves pollutant uptake or bounding by plants. The use of amendment prepared from organic source to increase soil fertility has been well recognized. The amendment not only provide plant nutrient which aids pollutant uptake but also result in hygienic disposal of organic waste, which otherwise may cause pollution problems. This paper is the first of a four part work which aims at comparing the effectiveness and use of three different amendments in phytoremediation of CCA polluted environment. The contamination and pollution of soils within the premises of Bendel Wood Treatment factory by Cu, Cr and As has been reported (Uwumarongie et al., 2008). This factory is our study site.

MATERIALS AND METHODS

Study site

The choice of this study site, the Bendel Wood Factory located at Ekenwan road, Benin City, Edo State was due to an earlier work (Uwumarongie et al., 2008). The factory treats wood used as poles for distributing electricity. The main chemical used by the factory is chromated copper arsenate (CCA).

Soil

Soil samples were collected from areas of known contamination. Plastic spade was used to collect soil from a depth not deeper than topsoil (0 - 15 cm) into polythene bags. A composite of all the samples was made, thoroughly mixed in a large polythene spread. It was then taken to the laboratory in two big polythene bags. A laboratory sample of 20 g was taken from the composite sample, air dried, and crushed to pass through a 2 mm sieve and stored in a polythene bag. This was used for the various analyses.

Poultry droppings

Poultry droppings were collected with a plastic spade inside a polythene bag from a poultry farm at Kwale. All non compostable materials in the waste were sorted out, thrown away and not included in the compost preparation. The nutrient content of the poultry dropping was determined to be; N = 0.186 ± 0.009%, P = 0.761 ± 0.007%, K = 0.130 ± 0.001%, Ca = 5.27 ± 0.099% and Mg = 1.52 ± 0.00%.

Maize grain

The maize grain used for the study was obtained from Edo State Ministry of Agriculture, Sapele Road, Benin City.

Pot experiment/germination studies

2 kg of the thoroughly mixed CCA polluted soil containing 2, 5, 10 and 20% of amendment were placed in plastic pots. Mixed thoroughly, watered and left for 2 weeks to stabilize before maize was planted. Control was set up without amendment. Maize seedlings (*Zea mays*) were soaked in water for 5 h and the viable ones sown in the plastic pots. Maintenance was carried out by watering using tap water when necessary. All experiment is in triplicates and result reported as mean plus standard deviation.

Total concentration of As, Cr and Cu in CCA contaminated soil

5 ml of aqua regia and 1 ml of perchloric acid were added to 1 g of soil sample in a 150 ml digestion tube and digested on a heating digester until white fumes of perchloric acid appeared. The tube was cooled and the sides rinsed with distilled water and then filtered through a Whatman 1 filter paper into a 100 ml volumetric flask. The volume was made up with distilled water (Tessier et al., 1979). The concentrations of the heavy metals in the various extracts were determined in a pre-calibrated AAS.

Sequential chemical speciation

A modified (Tessier et al., 1979) sequential extraction procedure modified by Salbu and Oughton (1998) was used to separate the metals into six operationally defined fractions. 2 g of the prepared soil sample was weighed and placed in a 100 ml polypropylene bottle. The sequential extractions were made into six various fractions as shown in Table 4. Table 3 is a summary of the methods and chemicals used.

Soluble fractions: 20 ml of distilled water was added to the soil sample in the polypropylene bottle and the mixture was shaken for 1 h. The mixture was then centrifuged at 1500 rpm for 15 min. The supernatant was filtered into a polypropylene bottle for metal analysis, while the residue was used for the next extractions.

Exchangeable fractions: 20 M of 1ml NH_4OA_C was added to the residue and the pH adjusted to pH 7 with ammonium hydroxide solution and agitated for 2 h. Again the process of separating the liquid from the mixture was carried out.

Carbonate-bound fractions: 20 ml of 1 M NH_4OA_C was added to the residue and adjusted to pH 5 with concentrated acetic acid. The mixture was then agitated for 2 h. Again the process of separating the liquid from the mixture was carried out.

Fe-Mn oxides bound fractions: 20 ml of 0.04 M $NH_2OH.HCl$ in

Table 1. Physicochemical properties of the soils.

Parameters	Control (no amendment)	2% amendment	5% amendment	10% amendment	20% amendment
pH	6.20 ± 0.40	6.56 ± 0.00	6.96 ± 0.90	6.98 ± 0.60	6.99 ± 0.50
OC%	1.24 ± 0.30	2.48 ± 0.60	3.14 ± 0.00	3.42 ± 0.40	3.78 ± 0.50
OM%	2.15 ± 0.40	4.29 ± 0.50	5.43 ± 0.20	5.92 ± 0.00	6.54 ± 0.40
Calcium (Meq/100 g)	5.68 ± 0.40	19.30 ± 1.00	19.60 ± 0.50	19.74 ± 0.60	20.20 ± 1.00
Magnesium (Meq/100 g)	1.96 ± 0.30	9.70 ± 0.60	9.78 ± 0.90	9.85 ± 0.80	9.90 ± 1.20
Sodium (Meq/100 g)	0.19 ± 0.10	0.22 ± 0.06	0.28 ± 0.08	0.30 ± 0.04	0.35 ± 0.03
Potassium (Meq/100 g)	0.57 ± 0.10	0.66 ± 0.20	0.68 ± 0.10	0.70 ± 0.20	0.75 ± 0.30
CEC (Meq/100 g)	8.40 ± 0.10	29.88 ± 0.30	30.44 ± 0.40	30.59 ± 0.60	31.20 ± 0.40
Phosphorus (mg/Kg)	44.74 ± 3.73	68.20 ± 2.70	68.80 ± 3.00	68.90 ± 3.10	69.40 ± 4.23
Nitrogen %	0.34 ± 0.08	0.89 ± 0.10	0.91 ± 0.10	0.97 ± 0.20	1.12 ± 0.40
Clay %	24.80				
Silt %	2.10				
Sand %	73.10				

OC = Organic carbon, OM = organic matter, and CEC = cations exchange capacity.

25% HOA_C was added to the residue and placed in a water bath for 6 h at 60°C. It was brought out and the process of separating the liquid from the mixture was carried out.

Organically bound fractions: 15 ml of 30% H_2O_2 adjusted with HNO_3 to pH 2 was added to the residue and heated for 5.5 h in a water bath at 80°C. After cooling, 5 ml of 3.2 M NH_4OAC in 20% HNO_3 was added; sample was shaken for 30 min and finally diluted to 20 ml with distilled water. Again the process of separating the liquid from the mixture was carried out.

Residual fractions: 5 ml of nitric acid and 1 ml of perchloric acid were added to 1 g of residue in a conical flask and heated on a hot plate at 60°C for 6 h. After evaporation, 1 ml of 2 M HNO_3 was added and the residue after dissolution was filtered through Whatman No 1 filter paper and into a 100 ml volumetric flask and diluted with distilled water to the mark. Note: All the solid phases were washed with 10 ml distilled water before the next extraction step. The washings were filtered with Whatman No 1 filter paper and added to the previous supernatant fraction and analyzed.

Uptake of As, Cr and Cu by maize

Plants were harvested 20 days after germination, rinsed with deionized water, cut into pieces, dried for two days at 80°C. It was then ashed in a Muffle furnace at 500°C for 6 h. The ash was dissolved in 20% nitric acid. The concentrations (mg/kg) of the metals in the dry weight of plant samples were determined by AAS Bulk Scientific VGP 210.

RESULTS AND DISCUSSION

Table 1 shows the physicochemical properties of the soil. The pH and organic carbon increased with the level of amendment. Incorporation of carbon-rich composts into soils has been shown to increase metal solubility through formation of soluble metal organic complexes (Zhou and Wong, 2001). The use of amendment especially at 20% level raised the pH level of the soil sample from 6.20 to 6.99. This increase of pH helps to bind the toxic metals which in itself is cleanup and also ensures that the soluble ones are not concentrated enough to cause much damage to the plants. It was established that near neutral pH generally results in micronutrient cations to be soluble enough to satisfy plant needs without becoming soluble enough as to be toxic (Brady and Well, 2005). It was also established that pH and microbial activity are most important factors which affect arsenic mobility and bioavailability in soils (Turpeinen et al., 1999; Xu et al., 1991). Also as the soil pH increases, negative soil surface charge is increased, which facilitates desorption of arsenate anions (Xu et al., 1991). The table also shows that the nutrient content of the soil increased dramatically (Ca: 5.6 to 20.2, K: 0.57 to 0.75, P: 44.74 to 69.40 and N: 0.34 to 1.12). The capacity of the soils to exchange cations (CEC) also increased. This is a condition that is favorable in phytoremediation. This reduced solubility keeps the plants alive over a longer period of time to do their work of cleanup.

Table 2 shows the total concentration of the metals in the soil as compared with their intervention values. Though total metal concentration do not necessarily correspond with metal availability and mobility, nations and corporate bodies around the world have placed standards for target and intervention levels based on total concentrations. Intervention values indicate that remediation action should be triggered, if soil metal concentration exceeds limit specified. From the values in Table 2, it is clear that the soil is polluted with regards to the three metals under study as concentrations of chromium, copper and arsenic are all higher than their intervention values. The use of DPR guideline (1991) given as shown below was used to calculate the intervention value for the soil.

$$I_C = \frac{Ist \cdot A + B \cdot \%CLAY + C \cdot \%OM}{A + B \cdot 25 + C} \qquad (1)$$

Table 2. Total concentration of the metals in soil sample/intervention values set by DPR.

Metals	Amount (mg/Kg)	Intervention values (mg/Kg)
Chromium	265.84 ± 33.0	190.52
Copper	155.82 ± 12.98	79.61
Arsenic	32.09 ± 2.48	28.82

Table 3. Extractants used in sequential speciation.

Step	Soil phases	Extract ant	Agitation time
1	Soluble fractions	20 ml distilled water	1 h 20°C
2	Exchangeable	20 ml NH_4OAc (pH 7)	2 h
3	Carbonate-bound	20 ml NH_4OAc (pH5)	2 h
4	Fe-Mn oxide bound	20 ml $NH_2OH.HCl$	6 h at 60°C
		15 ml of 30 % H_2O_2 (pH 2 HNO_3)	5.5 h at 80°C
5	Organic bound	After cooling, 5 ml 3.2MNH_4O acid in 20% HNO_3 Then dil. 20 ml with water	30 min
6	Residual	5 ml HNO_3 + 1 ml HClO After cooling + 2 M HNO_3	6 h

where Ic = Intervention value applying for the soil being evaluated (mg/Kg), Ist = Intervention for the standard soil [55 mg/Kg for As, 380 mg/Kg for Cr and 190 mg/Kg for Cu], %Clay = measured % clay in the soil being evaluated = 24.80%, % Organic matter (OM) = measured % organic matter in the soil being evaluated = 2.13%, A, B and C = constants which depends on the substances.

As, A = 15, B = 0.4 and C 0.4.
Cr, A = 50, B = 2 and C = 0.0.
Cu, A = 15, B = 0.6 and C = 0.6.

Total concentration helps to estimate effects and potential risks associated with elevated elemental concentrations. The concentrations of the metals in the soil under study need clean-up if intended for agricultural purposes. The nutrient content of the poultry dropping was established as; N = 0.186 ± 0.009%, P = 0.761 ± 0.007%, K = 0.130 ± 0.001%, Ca = 5.27 ± 0.099% and Mg = 1.52 ± 0.00%. These are added values to the quality of the soil. Apart from enriching the soil a key to effective phytoremediation, especially phytoextraction, is to enhance pollutant phyto-availability and to sustain adequate pollutant concentrations in soil solution for plant uptake (Lombi et al., 2001). The lives of the plants were sustained through nutrient enrichment. The effect of the toxic metals which could have been injurious to the plants as exhibited in the control was cushioned by the amendment. The plants in the control were already dying with their leaves turning yellow. Table 3 summarizes the various extractants and conditions used in the fractionation. Table 4 shows how the metals are asso-ciated with the different fractions. From the perspective of risk assessment, the chemical forms or species, in which a metal is found in the environment, provides predictive insights on the mobility, bioavailability, and fate of the metal contaminant. Plant species and relative abundance and availability of necessary elements have a control on metal uptake. Plant uptake is dependent on movement of element from the soil to the plant root through the soil solution; the limiting step for elemental concentration in soil is usually from the soil to the root (Chaney, 1988). In order to estimate effects and potential risk associated with elemental species and association, we must identify the fractions that are bioavailable for incorporation into biota (bioaccumulation). The soluble, exchangeable and to some extent carbonate fractions are mobile and bioavailable. Metal species associated with organic, Fe-Mn oxide and residual fractions are not readily bioavailable. They are tightly held and bound. Their release into the soil solution depends on strong depletion of minerals' content of the soil solution, decomposition and oxidation of organic matter. Arsenic has its highest concentration in the exchangeable phase (9.75 mg/Kg). The exchangeable fraction is most likely to cause a release into the soil solution due to ion exchange. When exchanged with other cations, it goes into solution. It is then available for plant uptake through movement of element from soil solution to plant root. Thus arsenic can be mobile and bioavailable in the soil. The species of As associated with organic matter is low, 2 mg/kg or 7%. Metals associated with organic matter are either complexed or adsorbed. Thus they are tightly held and their release into the soil solution is slow. Only 7% of total arsenic is in this fraction and this means that most of the arsenic is in the form that can easily go into solution. Arsenic concentration in the residual fraction is 6.85 mg/kg or 22%. At lower pH this could also be released.

Table 4. Geochemical forms of the metals in the CCA contaminated soil.

Fraction	As (mg/Kg)		Cr (mg/Kg)		Cu (mg/Kg)	
	Mean	%	Mean	%	Mean	%
Water soluble	4.0 ± 0.3	12.9	13.1 ± 0.7	5.21	1.0 ± 0.1	0.66
Exchangeable	9.75 ± 0.15	31.4	19.83 ± 0.28	7.9	3.48 ± 0.08	2.3
Carbonate	5.0 ± 0.1	16.1	15.1 ± 0.5	6	8.8 ± 0.2	5.8
Fe-Mn oxide	3.3 ± 0.2	10.63	8.5 ± 0.7	3.38	12.5 ± 0.3	8.24
Organic	2.15 ± 0.25	6.92	38.8 ± 0.4	15.43	26.6 ± 0.3	17.54
Residual	6.85 ± 0.35	22.1	156.18 ± 4.03	62.1	99.3 ± 0.4	65.47
Total	31.05		251.57		151.68	

Table 5. Geochemical forms of arsenic metal in soil 20 days after phytoremediation.

As (mg/kg)	Control	2%	5%	10%	20%
Water soluble	1.90 ± 0.00	1.40 ± 0.20	1.34 ± 0.40	1.20 ± 0.30	0.90 ± 0.30
Exchangeable	5.40 ± 0.40	5.25 ± 0.40	5.10 ± 0.80	5.10 ± 0.00	4.30 ± 0.90
Carbonate	3.80 ± 0.90	3.60 ± 0.20	3.70 ± 0.60	3.50 ± 0.20	3.50 ± 0.40
Fe-Mn oxide	3.10 ± 0.90	3.09 ± 0.50	3.45 ± 0.40	3.10 ± 0.20	3.20 ± 0.50
Organic	2.20 ± 0.50	2.30 ± 0.30	2.10 ± 0.20	2.24 ± 0.40	2.10 ± 0.20
Residual	7.10 ± 0.70	7.08 ± 0.90	6.70 ± 0.80	7.10 ± 0.80	7.00 ± 0.00
Sum	23.50	23.12	22.89	22.74	22.00
Total	24.10 ± 1.30	24.06 ± 1.60	23.95 ± 1.10	24.12 ± 1.20	23.61 ± 1.00

Table 6. Geochemical forms of chromium metal in soil 20 days after phytoremediation.

Cr (mg/kg)	Control	2%	5%	10%	20%
Water soluble	13.10 ± 0.00	11.70 ± 0.40	11.55 ± 0.30	10.90 ± 0.70	9.50 ± 0.60
Exchangeable	19.80 ± 0.70	17.95 ± 0.90	17.80 ± 0.30	17.10 ± 0.50	16.70 ± 0.70
Carbonate	17.10 ± 0.60	16.80 ± 0.80	16.80 ± 0.50	16.20 ± 0.70	16.00 ± 0.60
Fe-Mn oxide	6.80 ± 0.20	6.60 ± 0.30	6.70 ± 0.70	6.60 ± 0.30	6.60 ± 0.30
Organic	39.40 ± 1.20	39.10 ± 1.10	39.10 ± 1.50	39.00 ± 1.30	39.00 ± 1.00
Residual	158.15 ± 1.80	158.10 ± 2.10	158.10 ± 2.00	158.10 ± 1.70	157.90 ± 2.00
Sum	254.35	250.25	250.05	247.90	245. 70
Total	257.30 ± 4.00	253.45 ± 3.90	253.11 ± 3.00	252.90 ± 1.30	251.88 ± 1.40

The pH of the soil is 6.20. The species of chromium that is associated with the soluble, exchangeable and Fe- Mn oxide fraction is low as shown in the table. Thus they may not be readily available and mobile. The bulk of it is in residual 156 mg/kg or 62% and organic 38.8 mg/kg or 15%. Most species of copper like chromium are tied to the residual fractions (65%), and organic 18%.Tables 5, 6 and 7 show the geochemical forms of each of the metals in the soil after 20 days of phytoremediation. A comparism of Table 4 with Tables 5, 6 and 7 indicates that after twenty days of germination (cleanup), the species of the metals associated with soluble, exchangeable and carbonate fractions reduced greatly. These reductions are remarkable because these are the fractions that have positive influence on metal bioavailability. A significant point of note is that their rate of reduction increased as the percentage of amendments in the soil increased. We observed insignificance changes in the amount of metals in the organic and residual fractions before and after amendment, a plausible explanation for that is that most species of Cr and Cu are adsorbed to the insoluble organic fraction and tightly bound residual fractions. Allison et al. (2000) reported that once in soil, the Cu component of CCA is arrested by exchange with the soil, even in sandy soils. Also previous work indicates that Cr (111) is the least mobile of the CCA components (Archer and Preston, 1994; Cooper and Ung, 1997). The relative mobility and bioavailability of trace metals associated with different fractions has a lot of influence on plant uptake of metals.

Table 7. Geochemical forms of copper metal in soil 20 days of phytoremediation.

Cu (mg/kg)	Control	2%	5%	10%	20%
Water soluble	1.70 ± 0.20	1.50 ± 0.00	1.50 ± 0.20	1.46 ± 0.40	1.30 ± 0.30
Exchangeable	3.75 ± 0.60	3.40 ± 0.30	3.20 ± 0.00	3.19 ± 0.40	3.10 ± 0.50
Carbonate	6.80 ± 0.80	6.10 ± 0.20	6.10 ± 0.00	6.08 ± 0.60	5.90 ± 0.80
Fe-Mn oxide	11.70 ± 1.00	11.70 ± 1.10	11.60 ± 0.50	11.47± 0.60	11.45 ± 1.00
Organic	19.40 ± 1.00	19.40 ± 1.60	19.38 ± 0.90	19.35 ± 0.80	19.35 ± 1.20
Residual	79.80 ± 1.40	79.70 ± 2.00	79.70 ± 1.00	79.60 ± 2.00	79.50 ± 2.30
Sum	123.15	121.80	121.48	121.25	120.60
Total	131.84 ± 3.10	130.40 ± 3.00	130.36 ± 4.20	130.30 ± 2.40	128.30 ± 3.00

Table 8. Initial concentration and percentage uptake of metals.

Metal	Initial mg/Kg	Percentage uptake of pollutants				
		Control	2% amendment	5% amendment	10% amendment	20% amendment
As	32.09	18.3	18.3	19.6	20.3	20.6
Cr	265.84	1.84	1.93	1.94	1.98	2.0
Cu	155.82	12.86	13.4	14.2	14.84	17.1

Metal content of poultry droppings: Only copper was detected with a concentration of 0.30 mg/Kg.

Bioavailability/mobility of arsenic, chromium and copper in the CCA contaminated soil

The bioavailability/mobility of metals in soils is assessed on the basis of absolute and relative content of fractions weakly bound to soil components. The relative index of metal mobility was calculated as a “mobility factor” (Cezary and Bal, 2001) using the equation below:

$$M_f = \frac{F_1 + F_2 + F_3}{F_1 + F_2 + F_3 + F_4 + F_5 + F_6} \times \frac{100}{1} \qquad (2)$$

where: M_f = Mobility factor. F_1, F_2, F_3, F_4, F_5, *and* F_6 represent the percentage geochemical forms of the metals in the CCA contaminated soil Table 4, but here corrected to the nearest whole numbers. Values from Table 4 when applied in equation 2 above, assigned mobility factor (M_f) values of 60 for arsenic, 19 for chromium and 8 for copper. Metal forms bound to carbonate fractions F_3 are relatively less mobile than soluble and exchangeable fractions.

The result shows that arsenic is potentially mobile and biologically available because of its high M_f value of 60. High M_f values are symptoms of relatively high liability and biological availability of heavy metals in soils (Ahumada et al., 1999; Karczewska, 1996). Chromium is relatively mobile with M_f value of 19 while the mobility of copper is low with an M_f value of 8. The high M_f of As may be attributed to the low organic matter of the soil (Rahman et al., 2004). The organic matter of the soil is 2.5%. The use of a modified sequential extraction (six steps) procedure which partitioned the metals As, Cr and Cu among six operationally defined fractions: F_1 (water soluble), F_2 (exchangeable), F_3 (carbonate), F_4 (Fe-Mn), F_5 (organic) and F_6 (residual), the bioavailability/ mobility of metals in soils as assessed on the basis of absolute and relative content of fractions weakly bound to soil components, has revealed that arsenic with a total concentration of 32.09 mg/kg in the soil which is the lowest in total concentration (Table 2) has the highest M_f value (60). This made it to be highly labile and bioavailable and consequently more dangerous than the other two metals Cr with an M_f value of 19 and Cu with an M_f value of 8. Table 8 shows the uptake of the metals by maize (*Zea mays*) plant in the amended soil and compares it with uptake in the control soil. More metals were taken up by plants in the soils with amendments than in the control. For each metal the uptake and accumulation of metal increased as the percentage of amendment was increased. Only copper with a concentration of 0.3 mg/kg was detected in the poultry droppings. This value put the amendment as free of metal contaminants. Incorporation of carbon-rich composts into soils has been shown to increase metal solubility through formation of soluble metal organic complexes (Zhou and Wong, 2001). Arsenic can be transformed to reduced organic forms through biomethy-lation by microbes over a wide range of pH (Turpeinen et al., 1999). These arsenic organic compounds have high mobility, enhancing their availability for plant uptake. Figure 1 compares the uptake of the different metals (As, Cr and Cu) after 20 days of phytoremediation in mg/Kg between the control and soil with 20% amendment. Figure 2 compares the percentage uptake of the metals after 20 days of cleanup between the control and soil with 20% amendment.

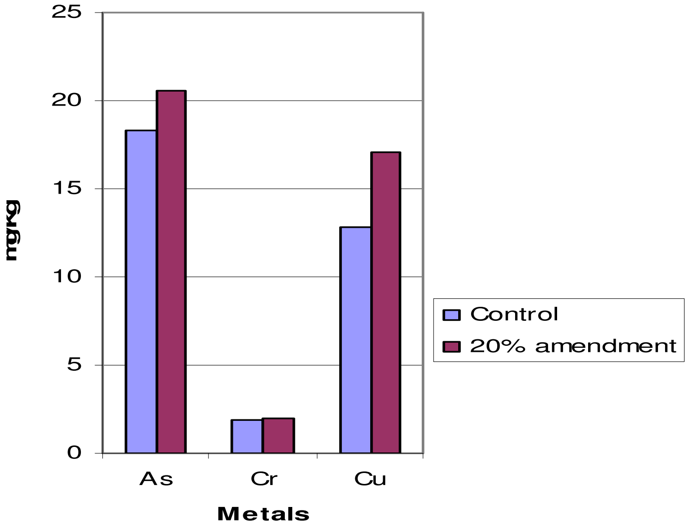

Figure 1. The uptake of the different metals (As, Cr and Cu) after 20 days of phytoremediation in mg/Kg between the control and soil with 20% amendment.

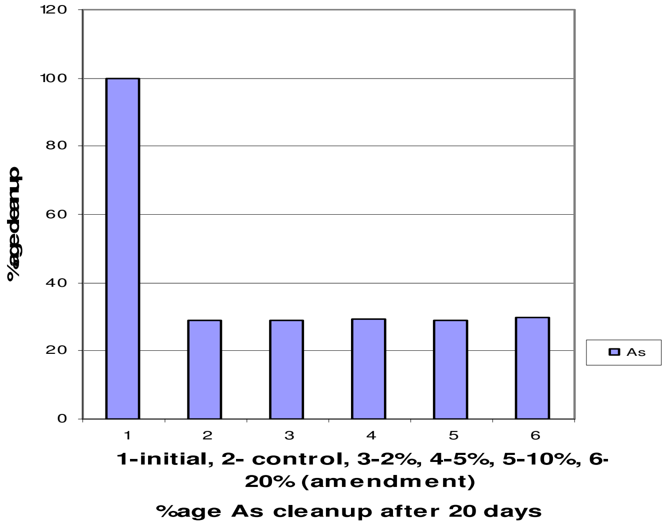

Figure 3. the percentage cleanup of the soil for As between the control and the different level of amendments.

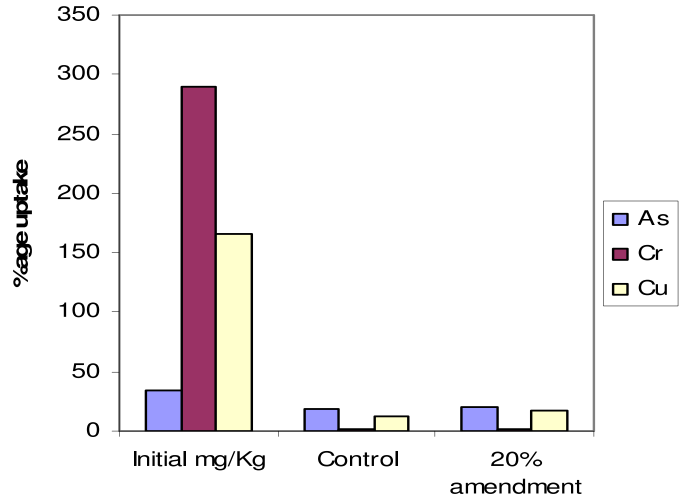

Figure 2. The percentage uptake of the metals after 20 days of cleanup between the control and soil with 20% amendment.

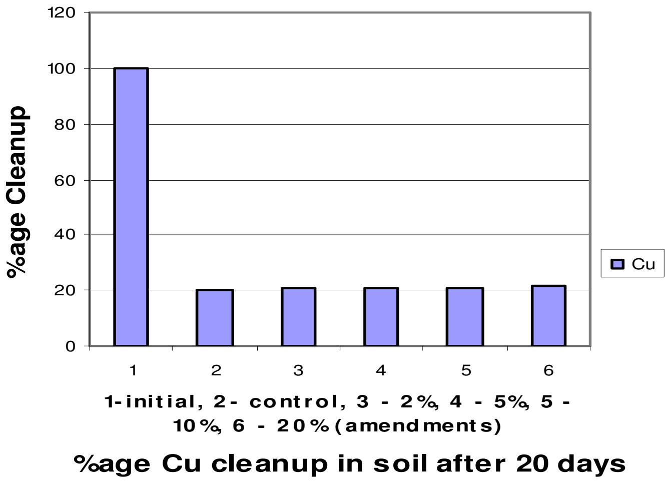

Figure 4. The percentage cleanup of the soil for Cu between the control and the different level of amendments.

Figures 3, 4 and 5 compare the percentage cleanup of the soil for the different metals between the control and the different level of amendments. A comparison of the result shows that arsenic, chromium and copper have average cleanup of 30, 20 and 12% respectively. The results indicate the usefulness of fowl droppings as an amendment to soil prior to phytoremediation of CCA contaminated soil.

Conclusion

This study has clearly confirmed that the soil is polluted if intended for agricultural purpose. After 20 days of phyremediation and at 20% amendment level the relative advantage in plant uptake was As 2.3%, Cr 0.16% and Cu 4.24% over the control. The rise in pH occasioned by the amendment also helps to bind the metals. The use of amendment which changed the character of the soil also enhanced phytostabilization through binding and reduced mobility. This reduced mobility prevents migration to the groundwater and consequently into terrestrial food webs. This use of amendment only provide plant nutrient which aids pollutant uptake but also result in hygienic disposal of organic waste, which otherwise may cause pollution problems.

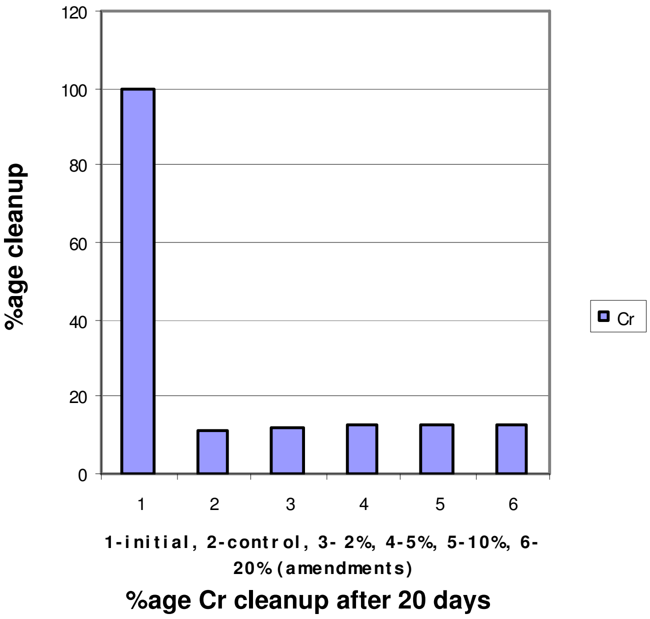

Figure 5. The percentage cleanup of the soil for Cr between the control and the different level of amendments.

REFERENCES

Ahumada I, Mendoza J, Asxar L (1999). Sequential extraction of heavy metals in soils irrigated with wastewater. Commun. Soil Sci. Plant Anal. 30: 1507-1519.

Allison G, Tyroczy NJ, Kelsall Y, Allinson M, Stagnitti F, Lloyd-Smith J et al (2000). Mobility of the constituents of chromate copper srsenate in a shallow sandy soil. NZ. J. Agric. Res. 43:146-9

Alloway BJ (1995). Heavy metal in soils. Vlackie Academic and Professional London.

Archer K, Preston A (1994). Dipletion of wood preservatives after four years marine exposure at Mt Maunganui harbor, NZ (IRG/WP94-50036). Stockholm: The International Research Group on Wood Preservation.

Cezary K, Bal RS (2001). Fractionation and mobility of copper, lead and zinc in the vicinity of a copper smelter. J. Environ. Qual. 30: 485-492.

Chaney RL (1988). Metal speciation and interaction among elements after trace element transfer in agricultural and environmental food chains, in Kramer JR, Allen HE, (eds) Metal speciation theory, Analysis and Application, Lewis Publications, Boca Raton, Fla. p 219-259.

Cooper P, Ung YT (1997). Environmental impact of CCA poles in service. 28th Annuaal Meeting of The International Research Group on Wood Preservative, 26-30May .Whistler, Canada.

Uwumarongie EG, Okieimen FE, Uwumarongie OH (2008). Phytoremoval of heavy metals from Chromated Copper Arsenate Contaminated Soil. J. Chem. Soc. Nig. 33(1): 126-131.

EG Uwumarongie, FE Okieimen, OH Uwumarongie (2008). Spatial uDistribution and Speciation of Arsenic, Chromium and Copper in Contaminated Soil. J. Chem. Soc. Nig., 33(1): 112-121.

El-Nady FE, Atta MM (1996). Toxicity and bioaccumulation of heavy metals to some marine biota from the Egyptian Coastal water. J. Environ. Sci. Health, A-31(7):529-1545.

Faisal MH, Hasnain S (2004). Microbial Conservation of Cr (VI) into Cr (III) in industrial effluent. Agric, J. Biotechnol. 3(11): 610-617.

Horsfall M, Jnr Spiff AI (2005). Effect of temperature on the sorption of Pb and Cd from aqueous solution by *Caladium bicolor* (wild ecosystem. Electrical J. Biotechnol. 8(2).

Igwe JC, Abia AA (2003), Cob and Husk as adsorbent for removal of Cd, Pb, and Zn ions from wastewater. The Physical Sci. 2:83-94.

Khodadoust AP, Reddy KR, Matun K (2005). Effects of different extraction agents of metals and organic contaminants removal from a field soil. J. Hazard. Mater. B117:15-25.

Karczewska A (1996). Metal specie distribution of top and subsoil in an area affected by copper smelter emission API. Geochem., 11:35-42.

Lombi E, Zhao, FJ, Dunham, SJ, McGrath SP (2001). Phytoremediation of heavy metal contaminated soils: Natural hyperaccumulation versus chemically enhanced phytoremediation. J. Environ. Qual., 30: 1919-1926.

Nagavallemma KP, Wani SP, Stephane L (2004). Recycling water into valuable organic fertilizer. Report no 8. Andhra Pradesh, India international Crops Research Institute for the Semi-Arid Tropics. p. 20.

Brady NC, Well RR (2005). Nature and Properties of Soils. Third Edition p. 33-34, 663.

Qun F, Shan X, Wei B (2004). Effect of low molecular weight organic acid and residence time on desoprtion of Cu, Cd and Pb, from soils. Chemosphere, 57:253-263.

Rahman FR, Allan DL, Sadowskey MJ (2004). Arsenic Availability from chromated Copper Arsenate (CCA). treated wood. J. Environ. Qual., 33: 173-180.

Salbu BTK, Oughton DH (1998). Characteristic of radioactive particles in the environment. Analyst 123:843-849.

Tessier A, Campbell PGC, Bisson M (1979). Sequential extraction procedures for the speciation of particulate trace metals. Anal. Chem. 51(7): 844-851.

Turpeinen R, Pantsar-Kallio M, Haggblom M, Kairesaalo, T (1999) Influence of microbes of the mobilization, toxicity and biomethylation of arsenic in soil. Sci. Total Environ. 236, 173-180.

Wani SP, Rupela OP, Lee KK (1995). Sustainable agriculture in the semi-arid tropics through biological nitrogen fixation in grain Legumes. Plant and soil 174: 29-49

Xu H, Allard B, Grimvall A (1991) Effects of acidification and natural organic materials on the mobility of arsenic in the environment. Water, Air and Soil pollution, pp. 57-58, 269-278.

Zhou LX, Wong JWC (2001). Effect of dissolved organic matter from sludge compost of soil copper sorption. J. Environ. Qual. 30: 878-883.