



Phytoremediation of chromated copper arsenate contaminated soil by maize (*Zea mays* L.)

Grace Esohe Uwumarongie-Ilori^{1*}, Felix Ebhodaghe Okieimen²

¹Agonomy Division, Nigerian Institute for Oil Palm Research, P.M.B. 1030, Benin City, Nigeria

²University of Benin, GeoEnvironmental Research Laboratory, Department of Chemistry, P.M.B. 1154, Benin City, Nigeria

Received: 28 February 2011

Revised: 25 March 2011

Accepted: 26 March 2011

Key words: Germination, contamination, maize, transfer.

Abstract

This study investigated the use of maize in removing arsenic, chromium and copper from chromated copper arsenate (CCA) contaminated soil in a pot experiment. Heavy metal levels in the CCA contaminated soil analysed showed high concentration of As, Cr and Cu. Total values of (39.55mg/kg) As, (313.97mg/kg) Cr and (200.00mg/kg) Cu were obtained in the CCA soil before planting. At the end of 60 days germination, the amount of the metals in the CCA contaminated soil reduced significantly ($P > 0.01$) accounting for 29% As, 3% Cr and 30% Cu of the initial concentration in the contaminated soil. Transfer factor and contamination factor were calculated to determine the accumulative factor of the metals in the plants and soils and this was used to interpret the state of the environment and ability of the maize to accumulate the metals. The contamination factor obtained for the chromated copper arsenate soil categorized the soil as highly contaminated while the transfer factors obtained for the various metals shows low metal accumulation in the plant.

*Corresponding Author: Grace Esohe Uwumarongie-Ilori ✉ esohe_grc@yahoo.com

Introduction

The assessment of pollutants in the environment is not enough an indication of its state of pollution without a serious consideration of such pollutants in biological systems. The assessment of bioavailability of pollutants in biological systems is a strong indication of their toxicity (Vutukutu, 2005; Waqar, 2006; Agunbiade and Fawale, 2009). In recent years, soil polluted by heavy metals has increased due to human activities and removal of such pollutants has also been of great concern (Uwumarongie et al., 2008; Fang et al., 2006; Waqar, 2006; Agunbiade and Fawale, 2009).

Arsenic, chromium and copper are common heavy metals found in wood treatment factory site. Heavy metals are not biodegradable and tend to accumulate in biological systems (Ozer and Pirincci, 2006; Uwumarongie et al., 2008; Kirpichtchikova, 2006). The environment has been found to absorb pollutants or clean up itself by natural biological/biochemical activities hence the increasing use of plants, plankton and other biota to remediate the environment (Agunbiade and Fawale, 2009; Hammains et al., 2006). Plants can accumulate and magnify trace pollutants like heavy metals to a level that is toxic to lives (Cabrera et al., 2006; Madejon et al 2006, Kumar et al., 1995; Qasem et al., 2006; Benhard and Neff, 2001). Although there are many known species of heavy metal hyper-accumulator plants (McIntyre and Glennis, 1997), in-situ successful application of hyper-accumulator has been limited because of their low biomass and specific growth needs

This study was conducted to investigate the use of maize in remediating heavy metals from CCA contaminated soil from wood treatment activities. CCA is used for treating wood to prolong its service life. Arsenic and copper in the CCA formulation inhibits insects and fungi respectively, while chromium is responsible for the fixation process, which binds CCA components to wood (Rahman et al., 2004). Chromium occurs naturally in the +3 oxidation state and produced in the +6 form by

anthropogenic activities. Cr in the +3 form is an essential nutrient in the body; useful in the metabolism of sugar, protein and fat (Okieimen and Uwumarongie, 2007). Arsenic occurs mostly as arsenate in oxygen-rich environments and well drained soil (H_2AsO_4^- in acidic soils and HAsO_4^{2-} in alkaline soils). In reducing environment, arsenic occurs as arsenite (+3) and arsine (-3) in strongly reduced environment (Ferguson, 1990). Arsenic may also exist in organo-metallic forms.

Materials and methods

Soil Sampling

Some physico-chemical parameters of the contaminated and control soil samples are given in Table 1. Chromated Copper Arsenate (CCA) contaminated soil was collected from the site of Bendel Wood Treatment Factory in Benin City, Edo State, Nigeria while the uncontaminated (control) soil sample was collected from a farmland, some distance from the wood treatment factory. The Bendel Wood Factory has been in operation for more than fifteen years. The wood treatment factory soil show great risk for the surrounding environment. The wood treatment factory is located about 500 metres north of Ogba river and the storm run-off water from the wood treatment factory drains into Ogba river and the river drains Benin City in a South Western direction. The Ogba River is a major source of domestic water supply to the Iyekogba community in the state capital. Ten grab samples were collected each from ten different locations at the topsoil depth of 0-10cm using a plastic trowel.

Experimental setup

The samples were thoroughly mixed by coning to make three replicate samples. All samples were analysed in duplicate for As, Cr and Cu. Four grains of pre-treated maize were sown in each pot (in triplicate) to a depth of 0.5cm and placed in a green house. Soils were watered as needed. The total levels of the metals in the contaminated soil (Table 2) indicate the

pollutional status of the soil and suggest remedial action (Uwumarongie, 2009)

Sampling and chemical analysis

The plants were left without watering for 1 day prior to harvest (60 days after germination). Plants were uprooted with the help of fine jet of water causing minimum damage to the roots, washed thoroughly with distilled water and blotted dry. The plants were cut into small pieces, mixed thoroughly and oven dried at 80°C. The oven-dried samples were ground and digested using nitric acid (analar grade). Soil samples were air-dried and sieved through a 2 mm sieve. 1g soil was digested with 5mL of aqua regia and 1mL of perchloric acid until the soil became grey and the digest made up to 1000mL. The metal contents were estimated using Atomic Absorption spectrophotometer, Bulk Scientific VGP 210. All reagents used were analytical grade and all glass wares were washed, soaked in nitric acid and washed in distilled water. Buck scientific standard solutions were used for the calibration and quality assurance for each analytical batch. Procedural blank samples were subjected to similar extraction method using the same amounts of reagents.

Data analysis

Statistical analysis was performed using SPSS statistical software. Contamination factor (CF) for soil and plant was calculated for the CCA contaminated soil to ascertain the level of contamination (Hakanson, 1980; Agunbiade and Fawale, 2009) by the chromated copper arsenate used in wood treatment. The contamination factor compares the concentration of metals in the surface layer to the background values by the expression

$$CF = C_a/C_n$$

Where, CF is the contamination factor (CF), C_a is the mean of the concentration of individual metal and C_n is the baseline or background concentration of the individual metal. The concentration of metals obtained for the uncontaminated soil (control) was

used as the baseline concentration. CF was defined according to four categories as follows:

$CF < 1$ - Low contamination factor

$1 < CF < 3$ - Moderate contamination factor

$3 < CF < 6$ - Considerable contamination factor

$6 < CF$ - Very high contamination factor

The transfer or bio-concentration factor (TF or BCF) of the metal into the plant was determined using the expression C_p/C_s where C_p is the concentration of the metal in plant and C_s is the concentration of the metal in corresponding soil. Transfer Factor (TF) greater than 1 indicates high level of accumulation of metals in the plant.

Results and discussion

The physico-chemical properties of the contaminated and control soil samples are given in Table 1. It can be seen that the CCA contaminated soil is moderately acidic (5.91) while the control soil is almost neutral (6.73). The acidic pH 5.91 of the contaminated soil is within the range for soil in the region but the near neutral pH (6.73) of the control soil is not within the range for soil in this region. Soil pH play a major role in the release of heavy metals as it controls the solubility and hydrolysis of metal hydroxides, carbonates and phosphates, ion-pair formation, solubility of organic matter, as well as surface charge of Fe, Mn and Al-oxides, organic matter and clay (Takalioglu *et al.*, 2006). The Cation Exchange Capacity was 50.77 ± 0.70 meq/100g. This value of CEC in the contaminated soil is high for the weathered soils (ultisols) of the Benin plains (Brandy and Well, 2005). Particle size showed that soil in the factory premises is sandy loam. The clay portion of the soil represents 26.08 % of soil component suggesting that the soil will have poor drainage ability and potentials for retaining harmful pollutants in the soil. The high total organic carbon content obtained in the contaminated soil ($3.15 \pm 0.37\%$) and control soil ($5.85 \pm 0.00\%$) may be due to the presence of degradable and compostable wastes in the soil samples (Mumoz, *et al.*, 1994).

Table 1. Physico-chemical characteristics of soil samples used in this study expressed as mean and standard deviation of soil dry weight.

Parameters	CCA contaminated soil	Control
pH	5.91 ± 0.10	6.73 ± 0.03
Clay (%)	26.08 ± 1.00	20.48 ± 0.0
Silt (%)	2.30 ± 0.00	2.00 ± 0.40
Sand (%)	71.62 ± 1.00	77.52 ± 1.00
Soil texture	Sandy loam	Sandy loam
Carbon (%)	3.15 ± 0.37	5.85 ± 0.00
Organic matter (%)	5.42 ± 0.30	10.06 ± 0.00
CEC (meq/100g)	50.77 ± 0.70	22.99 ± 0.01

Table 2. Levels of metals in the contaminated and control soil.

Metals (mg/kg)	Contaminated soil	Control soil
Copper (mg/kg)	200.00 ± 0.14	9.50 ± 0.50
Chromium (mg/kg)	313.97 ± 1.00	0.37 ± 0.15
Arsenic (mg/kg)	39.55 ± 0.21	0.35 ± 0.06

The amount of metals in the contaminated and control soil samples are given in Table 2. The values of 39.55 mg/kg arsenic, 313.97 mg/kg chromium and 200.00 mg/kg copper obtained for the CCA contaminated soil were higher than the values of 0.35 mg/kg arsenic, 0.37 mg/kg chromium and 9.50 mg/kg copper obtained in the control soil. Concentration of As, Cr and Cu in background or control soil sample were generally low except for Cu which had the highest concentration among the studied metals.

The amount of heavy metals in plant after 20 days germination is shown in Fig 1. The relative abundance of the metals in soil was found to be in the order of Cr > Cu > As while that of plant was Cu > As > Cr. Cu

was mostly accumulated in the maize plant than As and Cr.

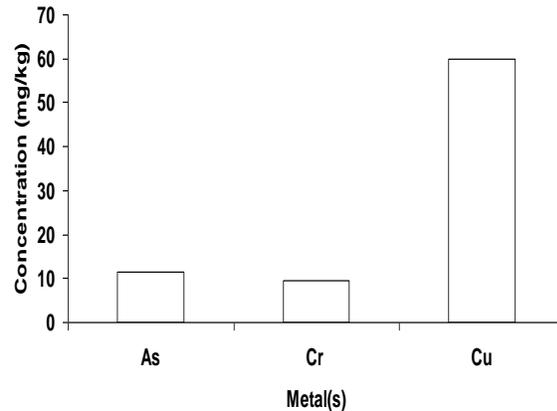


Fig 1. Amount of metal in maize after 20 days germination.

The CCA contaminated soil using the contamination factor equation is categorized as very highly contaminated ($6 < CF$) for both soil and plant. The metal values were also found to be higher than the intervention values of 28.81 mg/kg arsenic, 190.52 mg/kg chromium and 79.61 mg/kg copper provided in the Department of Petroleum Resources (DPR) guideline (1991).

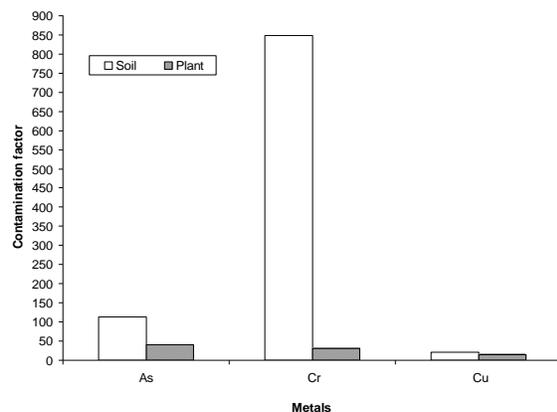


Fig 2. Contamination Factor of each metal in CCA contaminated soil and maize plant after 20 days germination.

The contamination factor of metals in soil and plant (Fig. 2) showed that Cr is the highest contaminant in soil followed by As. Amount of arsenic found in plant

was the highest of the three metals. Copper was the least contaminant in both soil and plant samples.

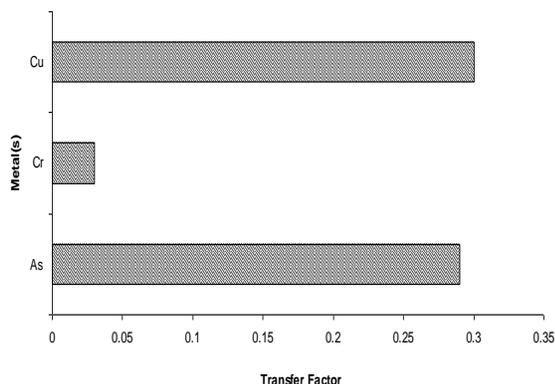


Fig 3. Graph of Transfer or bio-concentration factor of metals from soil to plant.

The transfer or bioconcentration factor (Fig 3) showed the rate of transfer of the metals from the CCA contaminated soil to maize plant. Cu had the highest transfer factor while Cr had the lowest transfer or bioconcentration factor. The result therefore shows the ability of maize in reducing the metal load in CCA contaminated soil

Conclusion

Heavy metal pollution caused by treating wood with chromated copper arsenate has been found to be significant. The values of TF obtained from this study in the absence of soil conditioner and amendment indicate a potential of maize as a bioremediation agent in accumulating As, Cr and Cu which are toxic to the ecosystem from such CCA contaminated soil

References

Agunbiade FO, Fawale AT 2009. Use of Siam weed biomarker in assessing heavy metal contaminations in traffic and solid waste polluted areas. *Int. J. Environ. Sci. Tech.* **6 (2)**, 267-276.

Brandy NC, Well, RR. 2005. The nature and properties of soils. Saurabh printers Pvt. Ltd, India. Thirteenth edition, 655-683.

Benhard T, Neff J. 2001. Metals bioavailability in the Navy's tiered ecological risk assessment process. Issue paper 1-15.

Cabrer, G, Perez R, Gomez JM, Abalos A, Cantero D. 2006. Toxic effects of dissolved heavy metals on *Desulfovibrio vulgaris* and *Desulfovibrio* sp. Strains. *J. Hazard. Mater* **135 (1-3)**, 40-46.

Department of Petroleum Resources, Lagos, 1991. Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN), 278-281.

Fang TH, Hwang JS, Hsiao SH, Chen HY. 2006. Trace metals in seawater and copepods in the ocean outfall area off the northern Taiwan coast. *Marine Environ. Res.* **61 (2)**, 224-243.

Ferguson JE. 1990. The heavy elements: chemistry environmental impact and health effects Pergamon Press, Oxford.

Hakanson L. 1980. An ecological risk index for aquatic pollution control. A sedimentological approach. *Water Res.* **14 (8)**, 975-1001.

Hammami A, Gonzalez F, Ballester A, Blazquez ML, Munoz JA. 2006. Biosorption of heavy metals by activated sludge and their desorption characteristics. *J. Environ. Manag.* **84 (4)**, 419-426.

Kirpichtchikova AT, Manceau A, Spadini L, Panfili F, Marcus MA, Jacquet T. 2006. Speciation and solubility of heavy metals in contaminated soil using X-ray micro fluorescence, EXAFS spectroscopy, chemical extraction and thermodynamic modeling. *Geochimica et Cosmochimica Acta* **70**, 2163-2190.

Madejon P, Murillo JM, Maranon T, Espinar JL, Cabrera F. 2006. Accumulation of As, Cd and

selected trace elements in tubers of *Scirpus maritimus* L. from Donana marshes (South Spain). *Chemosphere* **64** (5), 742-748.

McIntyre T, Glennis ML. 1997. The advancement of phytoremediation as an innovative environmental technology for stabilization, remediation or restoration of contaminated sites in Canada: A discussion paper. *J. Soil Contam.* **6** (3), 227-241.

Mumoz M, Pena L, Halloroms JO. 1994. Use of an industrial by-product as a liming source. *J. Agriculture of the University of Puerto Rico*, 78, 3-4, 73-86.

Nanda PBA, Dushenkov VM, Raskin I. 1995. Phyto-extraction: The use of plants to remove heavy metals from soils. *Environ. Sci. Technol.* **29**, 1232-1238.

Okieimen FE, Uwumarongie EG. 2007. Comparison of two sequential extraction schemes for metal fractionation in chromated copper arsenate (CCA) contaminated soil. *Nig. J. Appl. Sci.* **25**, 13-21.

Ozer A, Pirincci HB. 2006. The adsorption of Cd(II) ions on sulphuric acid-treated wheat bran. *J. Hazard. Mater.* **137** (2), 849-855.

Rahman FA, Allan DL, Rosen CJ, Sadowsky MJ. 2004. Arsenic availability from chromated copper arsenate (CCA)-treated wood. *J. Environ. Qual.* **33**, 173-180.

Takalioglu S, Kavtal S, Gultekin A. 2006. Investigation of heavy metal uptake by vegetables growing in contaminated soil using the modified BCR sequential extraction method. *Intern. J. Environ. Anal. Chem.* **88**(6), 417-430.

Qasem MJ, Adnan MM, Mohammed AZ, Baheyah MM. 2006. Fractionation and sequential

extraction of heavy metals in the soil of scrapyard of the discarded vehicles. *Environ Monitoring and Assessment* **112**, 197-210.

Uwumarongie EG. 2009. Ph. D thesis. Assessment of heavy metal mobility in chromated copper arsenate (CCA) contaminated soil. University of Benin, Benin City, Nigeria. 86-88.

Uwumarongie EG, Igene HA, Ediagbonya TF. 2008. Assessment of heavy metal contaminated soil from automobile workshop in Benin City. *ChemTech J.* **4**, 90-95.

Uwumarongie EG, Okieimen FE, Uwumarongie EN. 2008. Effect of Oxalic acid and Malonic acid on Heavy Metals removal from CCA contaminated soil. *Chemtech J.* **4**, 30-37.

Uwumarongie EG, Okieimen FE, Uwumarongie OH. 2008. Spatial distribution and speciation of arsenic, chromium and copper in contaminated soil. *J. Chem. Soc. Nig.* **33**(1), 112-121.

Vutukuru SS. 2005. Acute effects of hexavalent chromium on survival, oxygen consumption, hematological parameters and some biochemical profiles of the Indian Major carp, *Labeo rohita*. *Int. J. Environ. Res. Public Health.* **2** (3), 456-462.

Waqar A. 2006. Levels of selected heavy metals in Tuna fish. *Arab J Sci. eng.* **31** (1A), 89-92.