

# Immobilization of As, Cr and Cu in CCA Contaminated soil using Laterite and Termitaria

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## ABSTRACT

*This study examined the effectiveness of laterite and termitaria (termite mound soil) to reduce subsurface metal mobility and availability to plant uptake in chromated-copper-arsenate (CCA) contaminated soil. The contaminated soil ( $M_{Total} = 447.16\text{mg/kg}$ ; As = 6.84%, Cr = 58.43% and Cu = 34.73%) was treated with various amounts (0.5, 2, 4, 6, 8 and 10wt%) of the amendment soils in laboratory pot experiments. Sequential extraction procedure and plant uptake studies with maize seedlings were carried out and used to evaluate the solubility, mobility and transfer coefficients of the metals in the contaminated soil in relation to the levels of amendment application. It was found that the mobile fractions (water-soluble, exchangeable and carbonate bound) of As, Cr and Cu in the contaminated soil were transformed in the unavailable (Fe-Mn oxide bound, organic matter complexed and residual) forms following treatment with the amendment soils. The relative mobility factor (immobilization index),  $M_f/M_f^0$  was found to decrease with increase in the level of amendment application, was higher for termitaria than for laterite and was Cu < Cr < As. The observed difference in immobilization effectiveness was explained in terms of the difference in the binding capacity, resulting from the physico-chemical properties and surface chemistry, of the amendment soils. Heavy metal uptake by maize generally reflected the soluble/mobile pool and decreased with increase in the levels of amendment application.*

## INTRODUCTION

Heavy metal pollution in soil is a widespread global problem, which may threaten ecosystems and humans health. Heavy metals cannot be destroyed by biogeochemical processes therefore contaminated site restoration relies on *in situ* and *ex-situ* remediation technologies, which include incineration, disposal in landfill, electro-remediation, bioleaching, phytoremediation, soil washing, etc.<sup>1</sup>. These soil remediation techniques are based on two principles: heavy metal mobilization, which aims at the enhanced removal of metals from the soil matrix; and metal immobilization, which decreases the mass transfer of the metal from the solid soil matrix (immobilization) into the soil solution. Because metal immobilization reduces mobility in the soil and availability to

environmental receptors, it has been developed as an efficient less invasive remediation

technique for large but moderately metal contaminated sites<sup>2</sup>. Many additives, (amendments) commonly alkaline- and phosphate-based materials, have been screened for their potential to immobilize heavy metals in soil<sup>3,4,5,5,7</sup>.

The aim of this work was to examine the effectiveness of termitaria (ant mound soil) and laterite in reducing the mobility, availability and uptake by maize seedling of As, Cr and Cu in chromated-copper-arsenate (CCA) contaminated soil. Although CCA has been restricted in wood meant for domestic applications in the USA since 2004 and

prohibited by the European Union, it remains the main chemical cocktail used in the treatment of wood in Nigeria. Termitaria are built of earth particles, cemented together, forming hard, brick-like materials that are resistant to weathering and difficult to pick<sup>8</sup>. These properties together with its abundance, it was thought, should make it amendable as low-cost amendment in fixing heavy metals in soil. Previous studies reported on the application of termitaria as a component of concrete mixture<sup>9</sup> and as filler in natural rubber compounds<sup>10</sup>. Laterite is a surface formation in hot and wet tropical areas which is rich in iron and aluminum developed from intensive, long-term weathering of the underlying parent rock. Laterite is not uniquely identified with any particular parent rock, geologic age, single method of formation, climate *per se* or geographic location. Laterite consists mainly of kaolin, goethite (HFeO<sub>2</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>) and gibbsite (Al<sub>2</sub>O<sub>3</sub>.3H<sub>2</sub>O); with the oxides of iron giving laterite its characteristic red-brown colour<sup>11, 12</sup>. Typical laterite is porous, silica-poor and clay-like. The high content of the oxides of iron and aluminum should make laterite a good binder of metal and suitable for use in metal immobilization in soils.

## EXPERIMENTAL

Surface soil (< 20cm) with elevated concentration of As, Cr and Cu (Table 1) was collected from an active wood treatment site in Benin City, Nigeria. The soil was air-dried and sieved (< 2mm) prior to use. Termitaria and laterite soil samples were collected from Benin City environ, air-dried, ground and screened through a size 60-mesh sieve. The measured physico-chemical properties of termitaria and laterite (amendment soil) are given in Table 2.

### *Chemical immobilization treatments*

The contaminated soil sample (1kg) was mixed thoroughly with each of the soil amendments

(mound soil and laterite) at 0.5, 2, 4, 6, 8 and 10wt% loading and then placed in bowls. The amended soil samples together with a control sample (contaminated soil with no amendment) were maintained at 40% water retention capacity of the soil and left to stand for 14 days.

Table 1: Physico-chemical properties and total metal concentration in CCA contaminated soil

Properties	
Physico-chemical properties:	
pH	5.91 ± 0.10
EC (µs km)	0.011 ± 0.01
Organic carbon (%)	0.32 ± 0.04
Organic matter (%)	0.55 ± 0.04
Ca <sup>2+</sup> (meq/100g)	5.68 ± 0.40
Mg <sup>2+</sup> (meq/100g)	1.96 ± 0.30
Na <sup>+</sup> (meq/100g)	0.19 ± 0.10
K <sup>+</sup> (meq/100g)	0.5 ± 0.01
CEC (meq/100g)	8.40 ± 0.01
P (mg/kg)	44.74 ± 3.73
N (%)	0.34 ± 0.08
Clay (%)	24.80 ± 1.01
Silt (%)	2.10 ± 0.08
Sand (%)	73.10 ± 2.01
As (mg/kg)	30.60 ± 2.60
Cu (mg/kg)	261.40 ± 3.80
Cu (mg/kg)	155.40 ± 1.90

### Chemical fractionation procedure

The Salbu and Oughton<sup>13</sup> method, a modified version of the Tessier's method was used to fractionate the soil samples into various geochemical forms; water-soluble, exchangeable, carbonate bound, Fe-Mn oxide bound, organic matter bound and residual forms. The chemical fractionation scheme is given in Table 3.

5	Bound to organic matter	30% H <sub>2</sub> O <sub>2</sub> (pH 2)	5.5hr at 80°C
		3.2M NH <sub>4</sub> OAc	30min
6	Residual	Concentrated HNO <sub>3</sub>	6hr

Table 2: Some physico-chemical properties of termitaria and laterite

Properties	Termitaria	Laterite
pH	6.66 ± 0.20	6.69 ± 0.40
Organic matter (%)	2.43 ± 0.10	1.65 ± 0.20
Ca <sup>2+</sup> (meq/100g)	2.80 ± 0.05	3.36 ± 0.00
Mg <sup>2+</sup> (meq/100g)	2.36 ± 0.10	2.72 ± 0.00
Na <sup>+</sup> (meq/100g)	0.33 ± 0.00	0.43 ± 0.10
K <sup>+</sup> (meq/100g)	0.18 ± 0.02	0.29 ± 0.03
Fe <sup>2+</sup> (mg/kg)	451.12 ± 2.10	453.33 ± 1.80
Mn <sup>2+</sup> (mg/kg)	0.65 ± 0.02	3.77 ± 0.00
Clay (%)	14.10 ± 0.30	19.10 ± 1.00
Silt (%)	9.30 ± 1.00	6.80 ± 0.00
Sand (%)	76.60 ± 1.40	74.10 ± 1.00

Table 3: Sequential extraction procedure

Steps	Fractions	Reagents	Duration
1	Water-soluble	Distilled water	1 hr
2	Exchangeable	1M NH <sub>4</sub> OAc (pH 7)	2 hr
3	Bound to carbonate	1M NH <sub>4</sub> OAc (pH 5)	2hr
4	Bound to Fe-Mn oxides	0.04M NH <sub>2</sub> OH.HCl	6hr at 60°C

### Plant uptake studies

Maize (*Zea mays* L.) grains were sterilized with 0.1% with mercuric chloride solution for 5min to avoid fungal contamination. Four grains were sown in each pot to a depth of 0.5cm in 1kg of the soil samples. No nutrients were added to the pots. The pots were watered on alternate days, and he plants were harvested 20 days after germination. The uprooted plants were washed free of adhering soil particles, cut into small pieces and dried at 80°C and powdered. A known amount of the powdered sample was ashed in a Muffle furnace at 500°C for 3h. The ashed sample was allowed to cool down and then was treated with 2% HNO<sub>3</sub>. The mixture was filtered into 100ml volumetric flask and made up to mark with distilled water. The As, Cr and Cu contents of the filtrate were determined by AAS

## RESULTS AND DISCUSSIONS

The contamination status of the composite soil sample from the wood treatment factory in terms of contamination factor C<sub>f</sub>, degree of contamination, C<sub>D</sub>, and pollution load index, PLI, are given in Table 4. The values of contamination indices, PLI > 1, 1 < C<sub>f</sub> < 800; 26 < C<sub>D</sub> < 170, classify the soil as moderately contaminated to highly contaminated [14]. It can be seen from the results that contamination due to As presents greatest environmental concern with values of C<sub>D</sub> and PLI of 168.65 and 102.22 respectively. The physicochemical properties of the soil (Table 4) suggest that the soil will be fairly well drained, with implications for the potential deleterious impact presented by storm-water run-off and/or run-on from the site on receiving water bodies;

surfacewater and groundwater respectively. The high risk level presented by soil in the site particularly to the Ogba River into which storm water run-off from the site drains requires that appropriate remediation strategy be developed for the site.

Table 4: Contamination status of composite soil sample from wood treatment site in Benin City

	Contaminated soil (mg/kg)	Control soil (mg/kg)	Target values (mg/kg)	Uncontaminated soil (mg/kg)	Contamination factor, $C_f$
As	30.60	0.35	29.0	1.50	87.43 <sup>a</sup> ; 1.06 <sup>b</sup> ; 20.4 <sup>c</sup>
Cr	261.40	0.35	100.0	100.0	746.86 <sup>a</sup> ; 2.61 <sup>b</sup> ; 2.61 <sup>c</sup>
Cu	155.40	9.50	36.0	50.0	16.36 <sup>a</sup> ; 4.32 <sup>b</sup> ; 3.11 <sup>c</sup>
$C_D$ , degree of contamination = $\Sigma C_f$					168.65 <sup>a</sup> ; 7.99 <sup>b</sup> ; 26.12 <sup>c</sup>
PLI, Pollution load index = $\sqrt[n]{C_{f1} \times C_{f2} \dots C_{fn}}$					102.22 <sup>a</sup> ; 2.29 <sup>b</sup> ; 5.49 <sup>c</sup>

$C_f = M_{contam}/M_{ref}$ ; *a* is with reference to control, *b* is with reference to target values and *c* is with reference to uncontaminated soil.

Contaminant solubility in soil solution and mobility are increasingly being used as key indicators of potential risk to environmental receptors. The values of relative index of metal mobility in soil,  $M_f$ , given was the ratio of the sum of water soluble, exchangeable and carbonate bound fractions of the metals, to the sum of the fractions of the metal in the soil for the samples

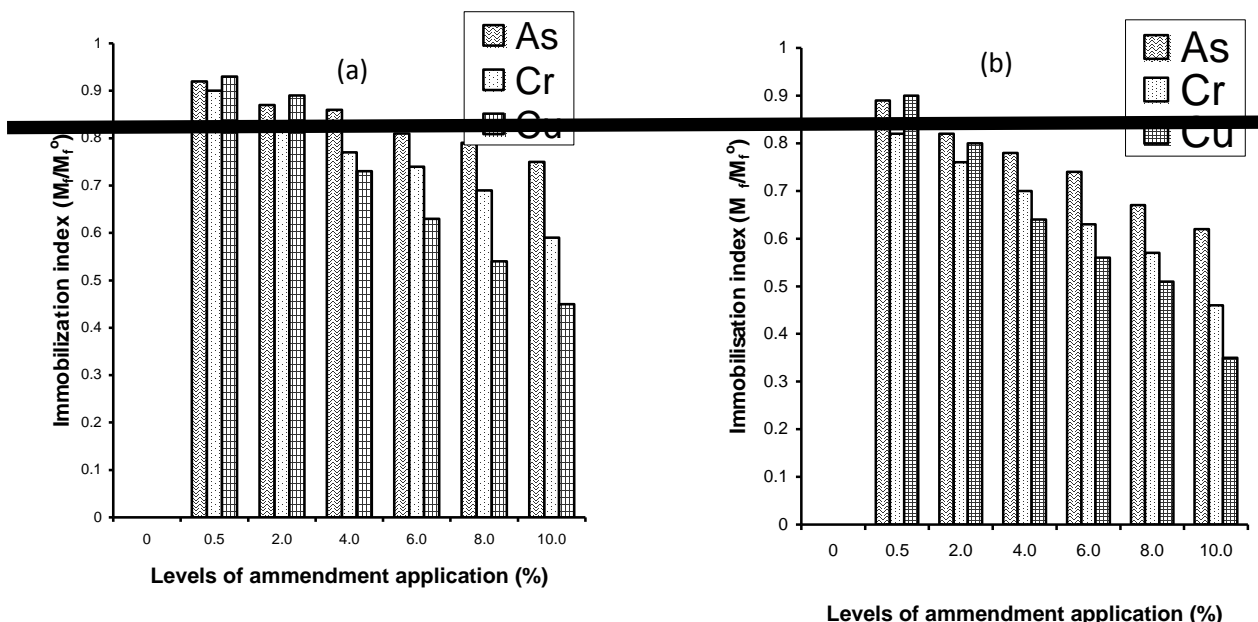
under study are given in Table 5. High  $M_f$  values are indicative of high mobility and potential availability of metals in soil. A soil treatment technique based on reducing the release and mobility/availability of metals in soil represents a less-invasive method of ameliorating the environmental impact of metals in contaminated soil. The effectiveness of soil amendment application in reducing subsurface mobility of metals in soil may be assessed from the immobilization index; the ratio of mobility factor of metals in amended soil  $M_f$ , to the value in uncontaminated soil  $M_f^0$ , ( $M_f/M_f^0$ ); the smaller the value of the index, the more effective the metal immobilization process.

Table 5: Mobility factor,  $M_f$  and concentration in soil solution  $C_s$  of As, Cr and Cu in CCA contaminated soil (unamended)

Metal	$M_f$ (%)	$C_s$ (%)*
As	67.14	23.16 <sup>a</sup> ; 15.54 <sup>b</sup>
Cr	21.95	26.28 <sup>a</sup> ; 5.77 <sup>b</sup>
Cu	14.04	14.61 <sup>a</sup> ; 2.05 <sup>b</sup>

\**a* = % in terms of mobile fraction; *b* = % in terms of total amount in soil

Figure 1 shows the variation of the values of immobilization index with levels of amendment application for laterite and termitaria. These results show a marked reduction in the mobility of the metals following amendment application with laterite being relatively more effective than termitaria in fixing the metals in the soil and apparent immobilization index for As > Cr > Cu. It was found from the chemical fractionation patterns of the metals that the Fe-Mn oxides fraction of the soil was responsible for most of the metal fixation. The contribution of the organic fraction of the amendments to metal immobilization was relatively smaller and resulted in about 25% increase in the amount of metals bound by their fraction. The observed trend in apparent immobilization effectiveness may be due to the difference in binding capacity of the amendment



soils arising from the physico-chemical properties and surface chemistry, e.g. relative metal oxides content.

Some suggested limitations of the immobilization technique in macrocosm (field application) remediation of contaminated soil

Figure 1: Immobilisation indices of CCA contaminated soil amended with (a) laterite and (b) termitaria

include concerns about the continuous retention of metals in soil where they become available to soil dwelling organisms that ingest soil particles, e.g. earthworm, and the potential release of immobilised metals at reduced pH which may occur over time, e.g. due to acid rain precipitation on contaminated soil<sup>15</sup>. The relatively high

metal oxides content, particularly Fe-Mn oxides content of the soil amendments used in this study whose metal binding capacities are little affected by pH suggests that metal re-mobilisation with time-bound decrease in soil pH may be insignificant and long-term reduction in metal mobility and in contaminated soil treated with laterite and termitaria would be feasible.

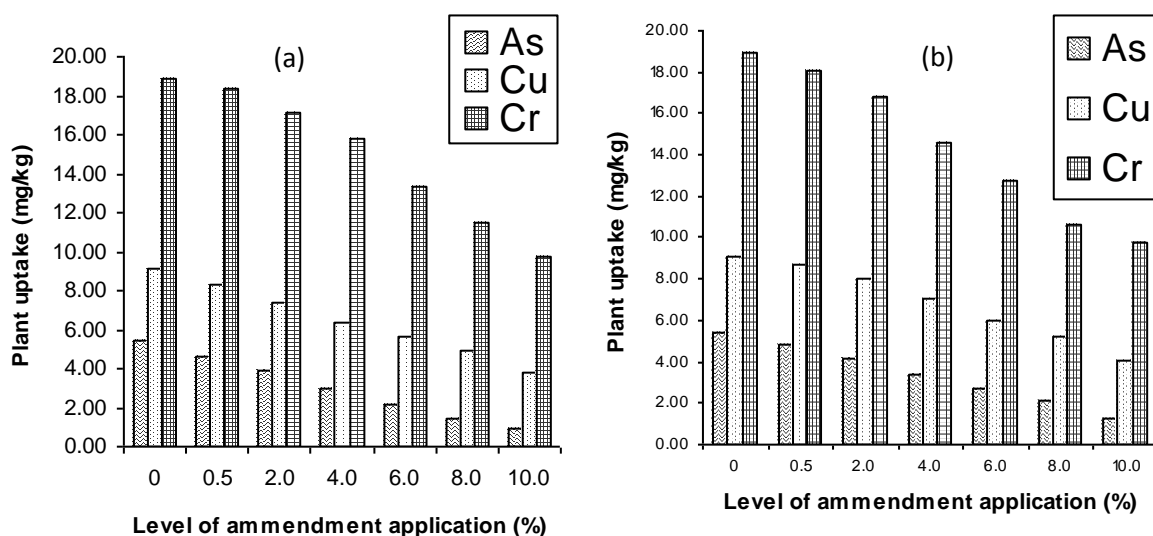


Figure 2: Variation of metal uptake by maize seedling with level of amendment (a) laterite (b) termitaria application

Figures 2 and 3 show the uptake levels and bioconcentration factor of As, Cr and Cu by maize seedlings in CCA contaminated soil respectively. The mechanism of phytoavailability of metals to plants in soil environment is a dynamic multi-stage process involving metal/solid soil phase – metal soil solution, metal soil solution – plant rhizosphere, metal exogenous root–metal/endogenous root, metal translocation stages [15]. A complex interplay of physical and biological factors at the plant root rhizosphere microenvironment determined the levels of metals uptake by plants.

It can be seen that the plant uptake levels decreased with level of ammendment application for both laterite and termitaria amended soil. The values of bioconcentration factor increase showed similar trend, decreasing with increase in ammendment application. These results are consistent with the reduced mobility/availability of the metals in the soil upon ammendment soil application. The relatively high values of metal uptake (up to 19mg/kg) and bioconcentration factor (up to 12% of the pseudo total levels of the metal in soil) make maize, a high biomass crop, a viable candidate plant for phytoremediation

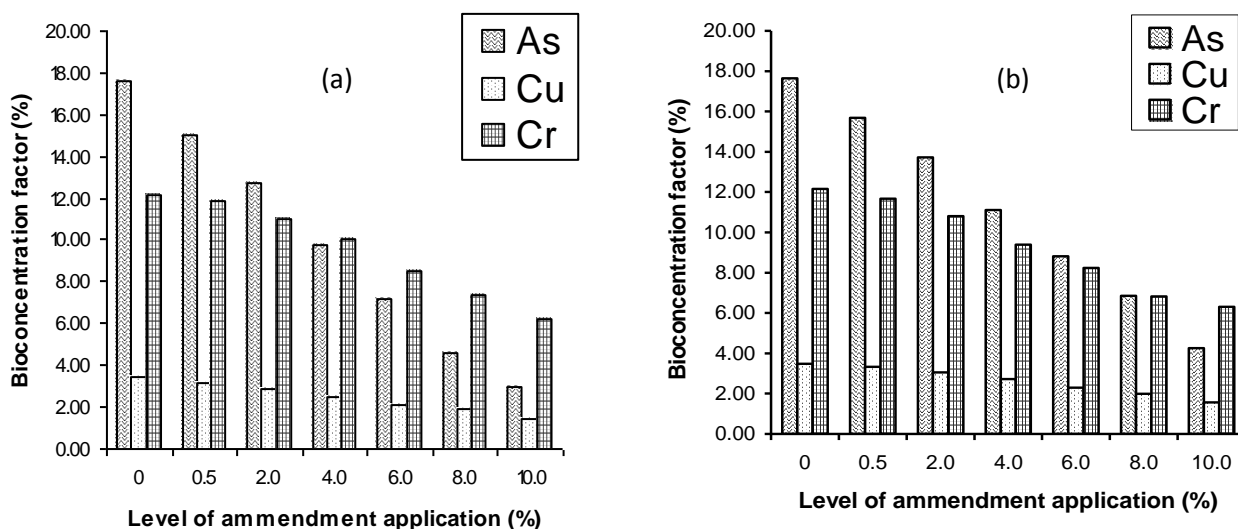


Figure 3: Bioconcentration of As, Cr and Cu by maize seedling grown on (a) laterite amended and (b) termitaria amended CCA contaminated soil.

### CONCLUSIONS

Laterite and termitira have been used as low-cost amendments in the remediation of CCA contaminated soil from a wood treatment site. Chemical fractionation of the amended soil revealed that a large proportion of the metals that are weakly bund to soil components was converted into the unavailable (Fe-Mn oxides bound, organic matter complexed and residual) forms following ammendment soil application. A potential for the application of laterite and termitaria in *in situ*

remediation of heavy metals contaminated soil is indicated from this study.

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