

# Contrasting effects of Corn cob and Cocoa pod husk biochars on Heavy metal Bioavailability, Speciation, and Uptake by Maize in a Mining-Contaminated soil

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## Abstract

Soil contamination by heavy metals (HMs) poses substantial risks to agricultural productivity and environmental health. Biochar, a carbon-rich material produced from organic waste, has been proposed as a soil amendment to lower HM bioavailability and enhance soil fertility. This study assessed the effects of cocoa pod husk biochar (CPHB) and corn cob biochar (CCB) on the bioavailability, speciation, and uptake of HMs (Cd, Cu, and Pb) by maize (*Zea mays* L.) in contaminated agricultural soil. A 60-day greenhouse experiment was conducted with biochar application rates of 1%, 2%, and 3% (w/w) at 70% field capacity. Soil properties such as pH, soil organic carbon (SOC), and cation exchange capacity (CEC) were analyzed before and after the experiment. HM bioavailability and speciation were determined using sequential extraction methods, while metal accumulation in maize roots and shoots was measured to calculate the bioconcentration factor (BCF) and translocation factor (TF). Biochar amendments raised soil pH, CEC, and SOC, with the most notable improvements observed in CPHB at 3%. The proportion of exchangeable HM fractions decreased relative to total content (Cd: by 5.12%, Cu: by 4.88%, Pb: by 3.89%), while residual fractions increased (Cd: by 58.14%, Cu: by 60.24%, Pb: by 52.11%), particularly at 2% and 3%. HM accumulation in maize roots and shoots significantly declined, with CPHB at 3% showing the greatest reduction. Correspondingly, the application of CPHB at 3% led to a decrease in BCF and TF values for Cd, Cu, and Pb, indicating diminished metal uptake by maize roots and limited translocation from roots to shoots. These findings suggest that CPHB, especially at a 3% rate, effectively reduces HM toxicity and bioavailability while promoting soil fertility, thus offering a promising strategy for remediating soils affected by mining activities.

**Keywords:** Biochar; Heavy metal immobilization; Sequential extraction; Bioconcentration factor; Agricultural remediation; Soil amendmen

## Introduction

Soil contamination by heavy metals (HMs) poses a significant threat to agroecosystem health, food security, and environmental sustainability, particularly in regions affected by artisanal and industrial mining (Wang et al., 2018). Toxic elements such as cadmium (Cd), copper (Cu), and lead (Pb) are persistent, non-biodegradable, and detrimental to living organisms, even at trace concentrations (Mishra et al., 2019). Once introduced into the environment, these metals undergo various geochemical processes that influence their distribution, speciation, and availability to plants, thereby impacting ecological risk and

food chain dynamics (Li et al., 2022).

In sub-Saharan Africa, particularly in Ghana, unregulated small-scale gold mining, locally termed “galamsey,” has resulted in severe HM contamination of arable soils (Ruiz-Huerta et al., 2022; Wongnaa et al., 2024). This poses a significant risk to the cultivation of maize (*Zea mays* L.), a staple crop essential for rural food security and livelihoods (Wongnaa et al., 2024). In contaminated soils, the fraction of metals available to plants is largely influenced by soil physicochemical attributes such as pH, cation exchange capacity (CEC), and soil organic carbon (SOC), as well as the specific chemical forms in which the metals are found (Eduah et al., 2022). Typically, exchangeable

and carbonate-bound fractions represent more bioavailable and mobile forms, while metals associated with residual or oxide-bound fractions exhibit limited mobility and lower ecological risk (Islam et al., 2023).

To address these challenges, biochar has emerged as a promising soil amendment for immobilizing HMs and enhancing soil quality (Eduah et al., 2022; Mazarji et al., 2023). Derived from the pyrolysis of biomass under limited oxygen conditions, biochar exhibits favourable surface characteristics, including high porosity, a substantial surface area, an alkaline pH, and diverse functional groups (Mazarji et al., 2023). These properties enable multiple immobilization mechanisms such as adsorption, ion exchange, complexation, and precipitation, which can effectively reduce metal bioavailability in contaminated soils (Liu et al., 2022). Moreover, biochar amendments can indirectly influence metal mobility by altering key soil parameters, particularly pH and CEC (Liu et al., 2022). The incorporation of biochar has also been shown to reduce concentrations of exchangeable metals, shift metal speciation into more stable fractions, and subsequently decrease plant metal uptake (Maharlouei et al., 2021; Rashid et al., 2022). The effectiveness of biochar in soil remediation is strongly dependent on its feedstock and pyrolysis conditions, which determine its chemical and structural attributes (Eduah et al., 2022). Although biochars produced from common agricultural residues such as rice husk, wheat straw, or poultry litter have been extensively studied (Hayat et al., 2021; Alarefee et al., 2023), less attention has been given to underutilized biomass sources such as cocoa pod husks (CPH) and corn cobs (CC), despite their abundance in West Africa. Ghana, as the second-largest global producer of cocoa, generates substantial quantities of CPH, often discarded as waste. Yet these materials possess distinct chemical profiles (e.g., high K and O content, low ash content) that may confer strong HM immobilization potential (Eduah et al., 2020).

Despite growing interest in biochar-based remediation, limited research has directly

compared the effects of different feedstock-derived biochars, particularly CPHB and CCB, on HM speciation and plant uptake under real-world conditions in mining-impacted soils (Gutiérrez et al., 2022; Tejada-Tovar et al., 2022). Understanding the interactions between biochar type, soil chemistry, and plant response is crucial for developing targeted remediation strategies. The study therefore aimed at assessing the effect of CC biochar and CPH biochar on the bioavailability, speciation and uptake of HMs (Cu, Pb and Cd) by maize in contaminated agricultural soil. Such integrated assessments are essential for validating biochar applications in complex, multi-contaminant soil systems.

## Materials and Methods

### *Soil and biochar*

Mining-contaminated agricultural soils were sampled at a depth of 20 cm from Nsuta-Tarkwa, Western Region, Ghana, an area severely impacted by artisanal and small-scale gold mining (ASGM). The study site lies within the moist semi-deciduous forest agroecological zone, which is typified by Ferric Acrisols according to the World Reference Base for Soil Resources (WRB, 1998; Dwomo and Dedzoe, 2010). This region has a mean annual rainfall ranging from 1,200 to 1,600 mm and mean annual temperatures between 26 and 28 °C (Dickson and Benneh, 1995). The soils are moderately acidic (pH = 5.40) and have a low soil organic carbon (SOC) content (1.30%) coupled with low CEC (8.40 cmolc/kg). The total Cd, Cu, and Pb in the soil are 3.50 mg/kg, 158.12 mg/kg, and 60.2 mg/kg, respectively, indicating that the soil used for the study was contaminated (Tóth et al., 2016).

Two biochar types, CCB and CPHB, pyrolyzed at 450 °C using Nabertherm furnace were obtained from the Council for Scientific and Industrial Research (CSIR), Ghana. The resulting biochars were finely ground to <1 mm using a mortar and pestle, dried at 105 °C and stored in air-tight bags for characterization

and greenhouse experiment.

#### *Soil and biochar analyses*

Particle size distribution was determined using the hydrometer method following Bouyoucos as described by Day (1965). The pH of both soil and biochar samples was measured in deionized water at a 1:2.5 (w/w) ratio after shaking for 1 hour, following the procedure outlined by Gaskin *et al.* (2008). The specific surface area of biochars was determined using the Brunauer-Emmett-Teller (BET) method (Gaskin *et al.*, 2008). CEC was determined using a modified ammonium acetate compulsory displacement method (Gaskin *et al.*, 2008). Total carbon of the biochar types was measured using a CHNS analyzer (Elementer vario El III, Germany) while the SOC was estimated by a modified Walkley and Black method (Walkley and Black, 1934). The total Cu, Pb and Cd were analyzed by digesting with concentrated HF-HNO<sub>3</sub>-HClO<sub>4</sub> acids (high purity) and measured using atomic absorption spectrometry (AAS, Perkin-Elmer 2380, USA).

#### *Greenhouse experiment*

A 60-day greenhouse pot experiment was conducted to evaluate the effects of CPHB and CCB on HM bioavailability and uptake by maize (*Zea mays* L.). The experiment followed a completely randomised design (CRD) with seven treatments (control, CPHB and CCB at 1%, 2%, and 3% w/w), each replicated three times. Plastic pots (5 L capacity; 22 cm height × 18 cm diameter) were filled with 4 kg of air-dried, sieved (≤2 mm) mining-contaminated soil, thoroughly mixed with the respective biochar, and pre-incubated for seven days. Soil moisture was maintained at 70% of field capacity using deionized water.

Surface-sterilized Obatanpa maize seeds were pre-germinated, sown (two per pot), and thinned to one seedling. Plants were grown under ambient greenhouse conditions (27-30 °C) with no fertiliser applied. At harvest (60 days), plants were separated into roots and shoots, rinsed, oven-dried at 65 °C, and weighed. Dried tissues were weighed for shoot

and root biomass and were further ground and digested with HNO<sub>3</sub>: HClO<sub>4</sub> (3:1 v/v) for HM analysis. Soil and biochar-amended soils were also analyzed for pH, CEC, SOC, total Cu, Cd, and Pb according to their respective methods described earlier.

#### *Sequential extraction for heavy metal speciation*

Sequential Cu, Pb and Cd extraction was conducted based on a modified protocol combining methods as described by Eduah *et al.* (2024) to separate HMs into six geochemical fractions: exchangeable (F1), carbonate-bound (F2), organic matter-bound (F3), amorphous Fe/Al-bound (F4), crystalline Fe/Al-bound (F5), and residual (F6). Aliquots of 1 g soil/ soil-biochar mixture were sequentially extracted with appropriate reagents under controlled pH, time, and agitation conditions. The extracts were filtered and quantified for Cu, Cd and Pb using AAS (Perkin-Elmer 2380).

#### *Heavy metal uptake, bioaccumulation factor and translocation factor calculation*

Total concentrations of Cd, Cu, and Pb in root and shoot tissues were determined following the procedures described by Munir *et al.* (2020) and Ruiz-Huerta *et al.* (2022). The bioconcentration factor (BCF) and translocation factor (TF) were calculated in accordance with the methods outlined in these studies, using the relationships:

$$BCF = \frac{HM \text{ concentration in the roots}}{HM \text{ concentration in the soil}} \quad (1)$$

$$TF = \frac{HM \text{ concentration in the shoots}}{HM \text{ concentration in the roots}} \quad (2)$$

#### *Statistical analysis*

All data were analysed using R software (version 4.3.0). Shapiro-Wilk and Levene's tests were used to verify normality and homogeneity of variances, respectively. One-way ANOVA was performed to assess treatment effects on HM speciation, uptake and maize biomass, followed by Tukey's HSD test for multiple comparisons ( $\alpha = 0.05$ ).

## Results and Discussion

### *Properties of the studied biochar and soil-biochar mixture*

Table 1 shows that both biochar types were strongly alkaline, with pH values of 9.1 for CPHB and 8.4 for CCB, reflecting the accumulation of basic oxides and carbonates during pyrolysis at 450 °C (Eduah et al., 2019). Alkaline biochars are known to neutralize acidic soils and immobilize HMs via precipitation and increased negative surface charge, thereby reducing metal solubility and mobility (Liu et al., 2022). EC values were moderately elevated, 1.20 dS/m for CPHB and 1.10 dS/m for CCB, indicating the presence of soluble mineral ions. These EC levels fall within acceptable thresholds for soil application and can enhance nutrient availability in nutrient-depleted tropical soils (Van Zwieten et al., 2010; Méndez et al., 2012).

CPHB had a slightly higher total carbon content (52.6%) than CCB (48.2%), likely due to the lignocellulosic composition of CPH feedstock (Singh et al., 2010). The high carbon content contributes to long-term organic matter stabilization and carbon sequestration (Singh et al., 2010). CEC was also higher in CPHB (38.2 cmol<sub>c</sub>/kg) than in CCB (31.7 cmol<sub>c</sub>/kg), suggesting greater capacity for HM retention. The specific surface area followed a similar pattern, with CPHB (220 m<sup>2</sup>/g) exceeding CCB (198 m<sup>2</sup>/g), indicating a greater density

of sorption sites (Chen et al., 2011).

Both biochars contained negligible levels of HMs: Cd was below detection limits, while Cu and Pb concentrations were <2.5 mg/kg and <1.5 mg/kg, respectively, well below critical thresholds for environmental safety (Tan et al., 2017), confirming their suitability for field application.

The application of both biochars significantly ( $p < 0.05$ ) improved soil chemical properties (Table 2). These changes included increased soil pH, SOC, CEC, and base cations, with more pronounced effects observed in CPHB treatments at 3% application rate. For instance, the soil pH increased from 5.4 in the control to 7.80 in the 3% CPHB treatment, a significant shift for HM-contaminated tropical soils, where low pH promotes HM solubility and bioavailability (Beesley et al., 2011). SOC and CEC also rose substantially, from 12.0 to 22.0 g/kg and from 12.8 to 28.0 cmol<sub>c</sub>/kg, respectively, under CPHB3%.

The increase in SOC reflects both the direct contribution of carbon-rich biochar and its indirect effect in stimulating microbial biomass and stabilizing native organic matter (Lehmann and Joseph, 2015). High SOC coupled with elevated CEC can support HM immobilization through electrostatic attraction and inner-sphere complexation, thereby reducing HM mobility and uptake by plants (Méndez et al., 2012). It is therefore expected that soils amended with CPHB could reduce HM availability and mobility.

**TABLE 1**

Properties of cocoa pod husk biochar (CPHB) and corn cob biochar (CCB)

Property	CPHB	CCB
pH (H <sub>2</sub> O)	9.1	8.4
Electrical conductivity (dS/m)	1.20	1.10
Total carbon (%)	52.6	48.2
CEC (cmol <sub>c</sub> /kg)	38.2	31.7
Specific surface area (m <sup>2</sup> /g)	220	198
Total Cd (mg/kg)	<DL	<DL
Total Cu (mg/kg)	<2.5	<2.5
Total Pb (mg/kg)	<1.5	<1.5

CPHB = cocoa pod husk biochar; CCB = corn cob biochar

**TABLE 2**  
Effect of biochar types at different rates on soil properties

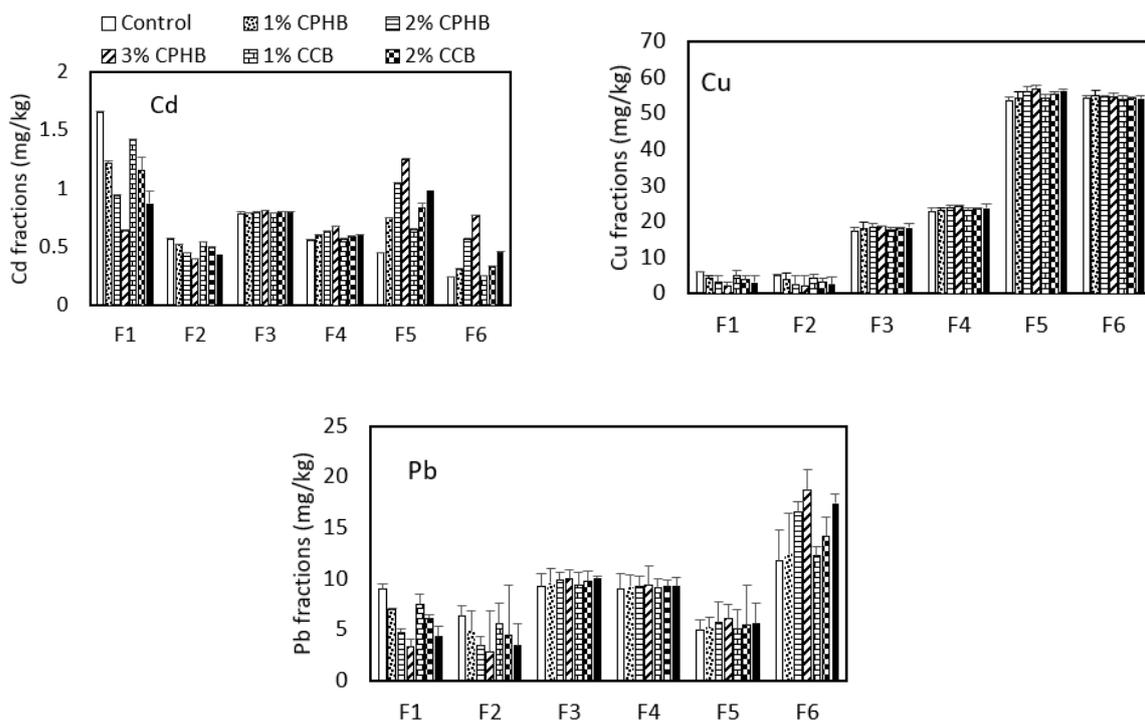
Treatment	pH (H <sub>2</sub> O)	SOC (g/kg)	CEC (cmol <sub>c</sub> /kg)
Control (0%)	5.40a	12.0a	12.8a
CCB 1%	5.95b	14.3b	15.6b
CCB 2%	6.30c	16.5c	18.0c
CCB 3%	6.55d	18.2d	20.1d
CPHB 1%	6.25c	15.8c	17.8c
CPHB 2%	7.10e	19.5e	25.0e
CPHB 3%	7.80f	22.0f	28.0f

Corn cob biochar (CCB) applied at 1%, 2% and 3%. Cocoa pod husk biochar applied at 1%, 2% and 3%. Different superscript letters within columns indicate significant differences ( $p < 0.05$ )

### Changes in heavy metal bioavailability and speciation

Heavy metal adsorption and lability in varying biochar-amended soils have been studied (Kumar *et al.*, 2021; Yu *et al.*, 2021). Reportedly, the binding state of HMs and, as such, their geochemical distribution in the solid phase of soils determines their extractability and mobility (Kumar *et al.*, 2021). In that regard, exchangeable HMs constitute the labile or readily available pool for plant uptake. Metals associated with carbonates are considered moderately labile. In contrast, HM associations with organic

matter, crystalline Fe and Al oxides, and amorphous Fe and Al oxides are typically more stable, requiring substantial changes in soil pH or redox conditions for release (Islam *et al.*, 2023). The residual fraction represents HMs in the highly stable or occluded form (Islam *et al.*, 2023). The speciation of Cd, Cu, and Pb across the six geochemical fractions (F1-F6) was significantly ( $p < 0.05$ ) influenced by biochar type and application rate (Figure 1). In the unamended control, the HMs were predominantly associated with labile fractions, Cd (F1+F2: 2.22 mg/kg), Cu (F1+F2: 10.72 mg/kg), and Pb (F1+F2: 15.25



**Figure 1:** Heavy metal (Cd, Pb and Cu) fractions in soil and biochar amended soils. Exchangeable (F1), carbonate-bound (F2), organic matter-bound (F3), amorphous Fe/Al-bound (F4), crystalline Fe/Al-bound (F5), and residual (F6)

mg/kg), implying high phytoavailability and environmental risk.

Biochar amendment significantly ( $p < 0.05$ ) reduced the proportion of metals in F1 and F2 and increased association with more stable fractions (F3-F6), especially under 2-3% CPHB. For example, CPHB 3% reduced Cd (F1+F2) from 2.22 to 1.04 mg/kg, while increasing Cd in F5+F6 from 0.69 to 2.02 mg/kg. Similarly, Cu and Pb showed a shift towards oxide-bound, organic-bound, and residual forms, indicating greater geochemical stability.

The enhanced metal retention in F5 (crystalline Fe/Al oxides) and F6 (residual) in CPHB treatments supports the hypothesis that CPHB, with its higher surface area, pH, SOC, and CEC, facilitates metal precipitation, complexation, and strong sorption. The higher SOC contributes reactive functional groups that complex metal ions, while increased CEC enhances electrostatic attraction and ion exchange, collectively reducing metal lability (Palansooriya et al., 2020). This reduction in metal mobility is largely attributed to changes in soil pH, which regulate the charge behaviour of organic functional groups (e.g.,  $-\text{COOH}$ ,  $-\text{OH}$ ) and the overall CEC, thereby strengthening metal complexation and adsorption (Eduah et al., 2024; Palansooriya et al., 2020). The effect was more pronounced in the 3% CPHB treatment, where a greater shift of metals into the stable F5 and F6 fractions was observed. The observed redistribution of metals from exchangeable and carbonate-bound forms (F1-F2) into

more stable fractions such as amorphous and crystalline Fe/Al oxide-bound (F3-F4), organic matter-bound (F5), and residual forms (F6) highlights the role of biochar in long-term metal immobilisation. These shifts are attributed to a combination of chemical and physical mechanisms, including pH-induced precipitation, electrostatic attraction, ion exchange, and surface complexation (Yu et al., 2021). As pH increases, several processes enhance metal retention in soils. Firstly, a higher pH elevates the negative surface charge, thereby strengthening the adsorption of positively charged metal ions, particularly in soils rich in variable-charge minerals such as those common in Ghana. Secondly, increased pH favours the hydrolysis of metal ions, leading to the formation of hydroxyl complexes (e.g.,  $\text{M}(\text{OH})^+$ ) that are more strongly bound to soil surfaces than free metal cations. Finally, metal precipitation as hydroxides (e.g.,  $\text{M}(\text{OH})_2$ ) further reduces their solubility and mobility within the soil matrix (Wang et al., 2009; Bolan et al., 2014; Palansooriya et al., 2020).

Although the total change in distribution across treatments was modest for some metals, the trend consistently showed reduced mobility and bioavailability in biochar-amended soils. CPHB was more effective than CCB, especially at higher doses, in stabilizing HMs and reducing their ecological risk.

#### *Effect of biochar on maize biomass production*

Amended heavy metal contaminated soils significantly ( $p < 0.05$ ) influenced maize

**TABLE 3**  
Dry root and shoot biomass of maize in soil and biochar amended soils

Treatment	Dry root biomass (g/plant)	Dry shoot biomass (g/plant)
Control (0%)	2.6a	8.4a
CCB 1%	3.1ab	9.8ab
CCB 2%	3.4b	10.5b
CCB 3%	3.6b	11.0b
CPHB 1%	3.5b	10.8b
CPHB 2%	3.9c	12.2c
CPHB 3%	4.3c	13.0c

Corn cob biochar (CCB) applied at 1%, 2% and 3%.  
Cocoa pod husk biochar (CPHB) applied at 1%, 2% and 3%. Different superscript letters within columns indicate significant differences ( $p < 0.05$ )

biomass accumulation (Table 3). Both root and shoot biomass increased significantly ( $p < 0.05$ ) with biochar application, with CPHB generally outperforming CCB significantly ( $p < 0.05$ ) across all rates. In the unamended soil, mean dry root and shoot biomass were 2.6 g/plant and 8.4 g/plant, respectively. The addition of CCB at increasing rates resulted in a significant ( $p < 0.05$ ) biomass enhancement, with shoot biomass rising to 11.0 g/plant at 3% application. Similarly, root biomass reached 3.6 g/plant under the same treatment. However, the most significant ( $p < 0.05$ ) improvements were observed in the CPHB treatments. At 3% CPHB, shoot biomass reached 13.0 g/plant increase over the control and root biomass was 4.3 g/plant, representing a 65.4% increase. The increment in plant growth in biochar-amended soils could be due to biochar's liming effect, especially CPHB, which neutralizes soil acidity and creates more favourable conditions for root development and nutrient uptake (Beesley *et al.*, 2011; Méndez *et al.*, 2012). More so, the increased CEC, particularly in CPHB, may improve nutrient retention and supply to plants over the growth period (Lehmann and Joseph, 2015). Additionally, the observed reductions in bioavailable HMs (Figure 1) likely alleviated metal-induced phytotoxicity, enabling improved physiological functioning and biomass accumulation (Luo *et al.*, 2020). Comparatively, the significant ( $p < 0.05$ ) impact of CPHB over CCB in promoting

maize growth is consistent with its higher SOC, surface area, and CEC (Table 1), all of which enhance its capacity to improve soil fertility and immobilize toxic elements. These findings align with earlier studies that reported enhanced biomass in metal-contaminated soils amended with high-quality biochars derived from nutrient-rich or lignocellulosic feedstocks (Singh *et al.*, 2010; Ahmad *et al.*, 2017).

#### *Heavy metal uptake in maize tissues*

The concentrations of Cd, Cu, and Pb in maize root and shoot tissues were significantly ( $p < 0.05$ ) influenced by biochar amendment type and application rate (Table 4). Across all treatments, a consistent trend was observed whereby increasing the rate of biochar addition, particularly CPHB, led to a significant reduction in HM accumulation in plant tissues. These findings align with the observations of Khan *et al.* (2020), who found markedly lower concentrations of Cu, Mn, Cd, and Pb in plant-based biochar-amended soils relative to the control.

In the unamended soil, maize roots accumulated 12.3 mg/kg Cd, 25.8 mg/kg Cu, and 30.5 mg/kg Pb, while corresponding shoot concentrations were 7.6, 15.0, and 18.2 mg/kg, respectively. These values indicate high bioavailability of HMs under contaminated conditions, with a strong likelihood of phytotoxic effects and potential transfer into the food chain.

**TABLE 4**

Heavy metal accumulation in roots and shoots of maize in soil and biochar-amended soils

Treatment	Root Cd (mg/kg)	Shoot Cd (mg/kg)	Root Cu (mg/kg)	Shoot Cu (mg/kg)	Root Pb (mg/kg)	Shoot Pb (mg/kg)
Control (0%)	12.3a	7.6a	25.8a	15.0a	30.5a	18.2a
CCB 1%	11.0ab	6.8ab	23.5ab	13.2ab	28.1ab	16.0ab
CCB 2%	10.0b	5.9b	21.3b	12.0b	25.6b	14.3b
CCB 3%	9.1b	5.1b	19.4b	10.8b	23.7b	13.5b
CPHB 1%	9.3b	5.4b	20.2b	11.4b	24.5b	13.9b
CPHB 2%	7.8c	4.0c	16.5c	8.9c	20.3c	11.1c
CPHB 3%	6.5c	3.2c	14.1c	7.1c	18.0c	9.2c

Corn cob biochar (CCB) applied at 1%, 2% and 3%. Cocoa pod husk biochar applied at 1%, 2% and 3%. *Different superscript letters within columns indicate significant differences ( $p < 0.05$ )*

Application of CCB at 1-3% (w/w) resulted in significant reductions in metal uptake. For example, root Cd and Pb concentrations declined to 9.1 and 23.7 mg/kg, respectively, at the highest CCB dose (3%). Similar reductions were observed in shoot tissues. However, CPHB proved more effective than CCB in limiting metal accumulation. At 3% CPHB, Cd, Cu, and Pb concentrations in shoots decreased by 57.9%, 52.7%, and 49.5%, respectively, compared to the control, with root concentrations showing similar declines.

The superior performance of CPHB may be attributed to its higher pH, surface area, and CEC, which promote metal immobilisation through multiple mechanisms, including pH-induced precipitation, surface complexation, ion exchange, and electrostatic adsorption (Beesley et al., 2011; Ahmad et al., 2017). Moreover, the presence of oxygenated functional groups (e.g.,  $-\text{COOH}$ ,  $-\text{OH}$ ) on CPHB surfaces enhances inner-sphere complexation of metal cations, resulting in stronger and more stable sorption (Chen et al., 2017).

The reductions in plant heavy metal concentrations are consistent with the observed shifts in soil metal speciation, where biochar treatments redistributed metals from exchangeable and carbonate-bound forms to less labile fractions, including Fe/Al- and organic matter-bound and residual forms (Section 3.2). Such transformations directly

lower metal bioavailability and consequently reduce plant uptake. The decline in metal accumulation may also be linked to the dilution effect associated with increased plant growth, metal immobilisation in soil, and the formation of stable metal-organic complexes (Xu et al., 2017). Additionally, the increase in soil pH induced by biochar addition contributes to decreased metal solubility and bioavailability (Eissa, 2024).

For comparison, permissible heavy metal concentrations in maize tissues (dry weight) are approximately 10-20 mg/kg for Cu, < 2 mg/kg for Pb, and 0.1-0.2 mg/kg for Cd (FAO/WHO, 2021). The concentrations observed under unamended conditions greatly exceeded the recommended limits for Pb and Cd in both roots and shoots, indicating severe contamination and potential food safety concerns. Notably, biochar treatments, particularly CPHB, substantially reduced these metal levels toward or below the permissible limits in shoot tissues, underscoring the strong potential of biochar to mitigate HM contamination and enhance food safety in contaminated soils.

#### *Bioconcentration and translocation of HMs in maize*

The BCF and TF of Cd, Cu, and Pb were significantly influenced by both the type and rate of biochar application (Table 5). The BCF quantifies the accumulation of metals in plant roots relative to soil concentrations, while TF

**TABLE 5**

Bioaccumulation factor and Translocation factor of heavy metals in soil and biochar amended soils

Treatment	Cd BCF	Cd TF	Cu BCF	Cu TF	Pb BCF	Pb TF
Control (0%)	2.67a	0.62a	1.35a	0.58a	0.50a	0.60a
CCB 1%	2.42a	0.62a	1.27a	0.56a	0.47a	0.57a
CCB 2%	2.21ab	0.59ab	1.15ab	0.56a	0.42ab	0.56a
CCB 3%	1.98b	0.56b	1.00b	0.56a	0.39b	0.57a
CPHB 1%	1.89b	0.58b	0.98b	0.56a	0.38b	0.57a
CPHB 2%	1.60c	0.51c	0.83c	0.54a	0.33c	0.55a
CPHB 3%	1.41c	0.49c	0.72c	0.50b	0.30c	0.51b

Corn cob biochar (CCB) applied at 1%, 2% and 3%. Cocoa pod husk biochar applied at 1%, 2% and 3%. *Different superscript letters within columns indicate significant differences ( $p < 0.05$ )*

reflects the efficiency of metal movement from roots to shoots (Ahmad *et al.*, 2017). In the control treatment (no biochar), Cd exhibited the highest BCF (2.67), followed by Cu (1.35) and Pb (0.50), indicating that Cd was the most readily accumulated by maize roots. Similarly, TF values ranged from 0.58 to 0.62, with Cd again showing the highest mobility from roots to shoots. These elevated BCF and TF values in the control underscore the high phytoavailability and mobility of HMs in unamended contaminated soils.

Application of CCB and CPHB significantly ( $p < 0.05$ ) reduced BCF values for all three metals, with greater reductions consistently observed under CPHB treatments. At the 3% CPHB rate, BCF values declined to 1.41 for Cd, 0.72 for Cu, and 0.30 for Pb. This stronger immobilizing effect of CPHB is attributed to its superior physicochemical properties, specifically its higher surface area, alkalinity, and abundance of oxygen-containing functional groups, which enhance metal adsorption, complexation, and precipitation (Beesley *et al.*, 2011; Ahmad *et al.*, 2017).

The TF values similarly declined with biochar application. For Cd, TF decreased from 0.62 in the control to 0.49 under 3% CPHB. Cu and Pb followed comparable patterns, with the lowest TF values recorded in the CPHB 3% treatment. These reductions suggest that biochar amendments limit root-to-shoot metal translocation, likely through enhanced metal sequestration in root tissues, reduced solubility in the rhizosphere, and possible inhibition of xylem loading (Wang *et al.*, 2020; Zhou *et al.*, 2023). This indicates a lower risk for contamination of the food chain and primary consumers (Puga *et al.*, 2016).

Across all treatments, Cd consistently exhibited higher BCF and TF values than Cu and Pb, reflecting its greater solubility and mobility in the soil–plant system. These findings align with previous studies on the effectiveness of biochar in reducing HM uptake and transport in plants grown in contaminated soils (Fellet *et al.*, 2014; Munir *et al.*, 2020). Clearly, both biochar types played a dual role as both a soil amendment for contaminant immobilization

and a plant growth enhancer in degraded environments. By limiting the uptake and internal transport of HMs in maize, biochar, especially from CPHB, offers a promising strategy for improving crop safety and productivity on mining-impacted agricultural lands.

## Conclusion

This study demonstrated that biochar amendments, particularly CPHB, significantly improved soil chemical properties, reduced HM bioavailability, and enhanced maize biomass in mining-contaminated soils. The application of CPHB at 2-3% w/w effectively shifted Cd, Cu, and Pb from labile (exchangeable) to more stable geochemical fractions (organic-bound, Fe/Al oxide-bound, and residual), thereby reducing their mobility and ecological risk. Correspondingly, HM concentrations in maize tissues decreased substantially with increasing biochar rate, particularly under CPHB, which also showed greater reductions in bioconcentration factor (BCF) and translocation factor values compared to CCB. These findings confirm the dual functionality of biochar, enhancing soil fertility while immobilizing toxic metals. Given its superior physicochemical properties, CPHB emerges as a more effective amendment than CCB for remediating mining-impacted agricultural lands and promoting safe crop production in tropical environments. Further field-scale studies are recommended to validate these results under long-term agronomic conditions.

## Reference

- Ahmad, M., Lee, S.S., Lee, S.E., Al-Wabel, M.I., Tsang, D.C. and Ok, Y.S.** (2017). Biochar-induced changes in soil properties affected immobilization/mobilization of metals/metalloids in contaminated soils. *Journal of soils and sediments*, **17**:17-730.
- Alarefee, H. A., Ishak, C. F., Othman, R. and Karam, D. S.** (2023). Effectiveness of

- mixing poultry litter compost with rice husk biochar in mitigating ammonia volatilization and carbon dioxide emission. *Journal of Environmental Management*, **329**:117051.
- Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J.L., Harris, E., Robinson, B. and Sizmur, T.** (2011). A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. *Environmental pollution*, **159(12)**:3269-3282.
- Bolan, N., Kunhikrishnan, A., Thangarajan, R., Kumpiene, J., Park, J., Makino, T., et al.** (2014). Remediation of heavy metal(loid)s contaminated soils- to mobilize or to immobilize? *Journal of Hazardous Materials*. **266**:141–166.
- Chen, B. and Yuan, M.** (2011). Enhanced sorption of polycyclic aromatic hydrocarbons by soil amended with biochar. *Journal of Soils and Sediments*, **11**:62-71.
- Chen, Y., Zhang, X., Chen, W., Yang, H. and Chen, H.** (2017). The structure evolution of biochar from biomass pyrolysis and its correlation with gas pollutant adsorption performance. *Bioresource technology*, **246**:101-109.
- Day, P. R.** (1965). Particle fractionation and particle-size analysis. In: Black, C.A. (Ed.), *Methods of Soil Analysis, Agronomy*, **9**:545–567.
- Dickson, K.B., Benneh, G.** (1995). *A New Geography of Ghana*, third ed. Longman, Essex.
- Dwomo, O. and Dedzoe, C. D.** (2010). Oxisol (ferralsol) development in two agro-ecological zones of Ghana: a preliminary evaluation of some profiles. *Journal of Science and Technology*. **30 (2)**:11–28.
- Eduah, J. O., Nartey, E. K., Abekoe, M. K., Asomaning, S. K., Essibu, J. K., and Henriksen, S. W.** (2022). Acidity and Aluminum Speciation in Biochar Amended Tropical Soils. *Communications in Soil Science and Plant Analysis*, **53(7)**:913–927.
- Eduah, J. O., Henriksen, S. W., Nartey, E. K., Abekoe, M. K. and Andersen, M. N.** (2020). Nonlinear sorption of phosphorus onto plant biomass-derived biochars at different pyrolysis temperatures. *Environmental Technology & Innovation*, **19**:100808.
- Eduah, J. O., Arthur, A., Dogbatse, J. A., Amoako-Attah, I. and Afful, E. A.** (2024). Ecological effects of soil physicochemical properties and copper speciation on the microbial properties associated with land use management in cacao production. *Environmental Technology & Innovation*, **33**: p.103538.
- Eduah, J. O., Nartey, E. K., Abekoe, M.K., Asomaning, S. K., Essibu, J. K., and Henriksen, S.W.** (2022). Acidity and aluminum speciation in biochar amended tropical soils. *Communications in Soil Science and Plant Analysis*. **53 (7)**: 913–927.
- Eduah, J. O., Nartey, E. K., Abekoe, M. K., Breuning-Madsen, H. and Andersen, M. N.** (2019). Phosphorus retention and availability in three contrasting soils amended with rice husk and corn cob biochar at varying pyrolysis temperatures. *Geoderma*, **341**:10-17.
- Eissa, R., Jeyakumar, L., McKenzie, D. B. and Wu, J.** (2024). Influence of Biochar Feedstocks on Nitrate Adsorption Capacity. *Earth*, **5(4)**:1080.
- FAO/WHO Codex Alimentarius Commission** "General Standard for Contaminants and Toxins in Food and Feed," CODEX STAN 193-1995, last amended 2021.
- Fellet, G., Marmiroli, M. and Marchiol, L.** (2014). Elements uptake by metal accumulator species grown on mine tailings amended with three types of biochar. *Science of the Total Environment*, **468**:598-608.
- Gaskin, J., Steiner, C., Harris, K., Das, K., Bibens, B.** (2008). Effect of low-temperature pyrolysis conditions on biochar for agricultural use. *Trans. ASABE (American Society of Agricultural and Biological Engineers.)* **51(6)**:2061–2069.
- Gutiérrez, E., Chávez, E., Gamage, K. H., Argüello, D., Galkaduwa, M. B. and Hettiarachchi, G. M.** (2022). Cadmium fractionation in soils affected by organic matter application: Transfer of cadmium

- to cacao (*Theobroma cacao* L.) tissues. *Frontiers in Environmental Science*, **10**: p.954521.
- Hayat, E. S., Andayani, S. and Hayati, R.** (2021). July. Substitution of inorganic fertilizer with organic fertilizer based on poultry waste combined with rice husk biochar. In IOP Conference Series: *Earth and Environmental Science* (Vol. 824, 1: p. 012038). IOP Publishing.
- Islam, M. M., Akther, S. M., Wahiduzzaman, M., Hossain, M. F., Parveen, Z.** (2023). Fractionation and contamination assessment of Zn, Cu, Fe, and Mn in the sundarbans mangrove soils of Bangladesh. *Soil and Sediment Contamination: An International Journal*. **32**(7):789–811.
- Khan, A. Z., Ding, X., Khan, S., Ayaz, T., Fidel, R. and Khan, M. A.** (2020). Biochar efficacy for reducing heavy metals uptake by Cilantro (*Coriandrum sativum*) and spinach (*Spinacia oleracea*) to minimize human health risk. *Chemosphere*, **244**: p.125543.
- Kumar, V., Pandita, S., Sidhu, G.P.S., Sharma, A., Khanna, K., Kaur, P., Bali, A.S., Setia, R.,** (2021). Copper bioavailability, uptake, toxicity and tolerance in plants: a comprehensive review. *Chemosphere* **262**: p127810.
- Lehmann, J. and Joseph, S.** (2015). Biochar for environmental management: an introduction. In *Biochar for environmental management* (pp. 1-13) Routledge.
- Li, Q., Wang, Y., Li, Y., Li, L., Tang, M., Hu, W., Chen, L., and Ai, S.** (2022). Speciation of heavy metals in soils and their immobilization at micro-scale interfaces among diverse soil components. *Science of the Total Environment* **825**: p153862.
- Liu, Z., Xu, Z., Xu, L., Buyong, F., Chay, T. C., Li, Z., Cai, Y., Hu, B., Zhu, Y. and Wang, X.** (2022). Modified biochar: synthesis and mechanism for removal of environmental heavy metals. *Carbon Research*, **1**(1): p.8.
- Luo, C., Yang, J., Chen, W. and Han, F.** (2020). Effect of biochar on soil properties on the Loess Plateau: Results from field experiments. *Geoderma*, **369**, p.114323.
- Maharlouei, Z. D., Fekri, M., Saljooqi, A., Mahmoodabadi, M. and Hejazi, M.** (2021). Effect of modified biochar on the availability of some heavy metal speciation and investigation of contaminated calcareous soil. *Environmental Earth Sciences*, **80**:1-20.
- Mazarji, M., Bayero, M. T., Minkina, T., Sushkova, S., Mandzhieva, S., Bauer, T. V., Soldatov, A., Sillanpää, M. and Wong, M. H.** (2023). Nanomaterials in biochar: review of their effectiveness in remediating heavy metal-contaminated soils. *Science of The Total Environment*, **88**: p163330.
- Méndez, A., Tarquis, A. M., Saa-Requejo, A., Guerrero, F. and Gascó, G.** (2013). Influence of pyrolysis temperature on composted sewage sludge biochar priming effect in a loamy soil. *Chemosphere*, **93**(4):668-676.
- Méndez, A., Tarquis, A. M., Saa-Requejo, A., Guerrero, F. and Gascó, G.** (2013). Influence of pyrolysis temperature on composted sewage sludge biochar priming effect in a loamy soil. *Chemosphere*, **93**(4):668-676.
- Mishra, S., Bharagava, R. N., More, N., Yadav, A., Zainith, S., Mani, S., Chowdhary, P.** (2019). Heavy metal contamination: an alarming threat to environment and human health. *Environmental Biotechnology for a Sustainable Future*, **103**–125.
- Munir, M. A. M., Liu, G., Yousaf, B., Ali, M. U., Abbas, Q. and Ullah, H.** (2020). Synergistic effects of biochar and processed fly ash on bioavailability, transformation and accumulation of heavy metals by maize (*Zea mays* L.) in coal-mining contaminated soil. *Chemosphere*, **240**: p.124845.
- Palansooriya, K. N., Shaheen, S. M., Chen, S. S., Tsang, D. C. W., Hashimoto, Y., Hou, D., et al.** (2020). Soil amendments for immobilization of potentially toxic elements in contaminated soils: A critical review. *Environmental International*. **134**: p105046.
- Puga, A. P., Melo, L.C.A., de Abreu, C. A., Coscione, A. R. and Paz-Ferreiro, J.** (2016). Leaching and fractionation of heavy metals in mining soils amended with biochar. *Soil and Tillage Research*, **164**:25-33.
- Rashid, M. S., Liu, G., Yousaf, B., Song, Y.,**

- Ahmed, R., Rehman, A., Arif, M., Irshad, S. and Cheema, A. I.** (2022). Efficacy of rice husk biochar and compost amendments on the translocation, bioavailability, and heavy metals speciation in contaminated soil: Role of free radical production in maize (*Zea mays* L.). *Journal of Cleaner Production*, **330**:129805.
- Ruiz-Huerta, E. A., Armienta-Hernández, M. A., Dubrovsky, J. G. and Gómez-Bernal, J. M.** (2022). Bioaccumulation of heavy metals and As in maize (*Zea mays* L) grown close to mine tailings strongly impacts plant development. *Ecotoxicology*, **31(3)**:447-467.
- Singh, B., Singh, B. P. and Cowie, A. L.** (2010). Characterisation and evaluation of biochars for their application as a soil amendment. *Soil Research*, **48(7)**:516-525.
- Tejada-Tovar, C., Villabona-Ortíz, A. and González-Delgado, Á.** (2022). Adsorption study of continuous heavy metal ions (Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>) removal using cocoa (*Theobroma cacao* L.) pod husks. *Materials*, **15(19)**: p6937.
- Tian, K., Huang, B., Xing, Z., Hu, W.** (2017). Geochemical baseline establishment and ecological risk evaluation of heavy metals in greenhouse soils from Dongtai, China. *Ecological Indicators*. **72**:510–520.
- Tóth, G., Hermann, T., Da Silva, M R. and Montanarella, L. J E.I.** (2016). Heavy metals in agricultural soils of the European Union with implications for food safety. *Environment International*, **88**:299-309.
- Van Zwieten, L., Kimber, S., Morris, S., Chan, K.Y., Downie, A., Rust, J., Joseph, S. and Cowie, A.** (2010). Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant and soil*, **327**:235-246.
- Wang Y, Shao Q, Huang S S, Zhang B, Xu C.** (2018). High performance and simultaneous sequestration of Cr(VI) and Sb(III) by sulfidated zerovalent iron. *Journal of Cleaner Production* **23**:27–31
- Wang, Y., Liu, Y., Zhan, W., Zheng, K., Wang, J., Zhang, C. and Chen, R.** (2020). Stabilization of heavy metal-contaminated soils by biochar: Challenges and recommendations. *Science of the Total Environment*, **729**: p.139060.
- Wongnaa, C. A., Nti, E. K., Acheampong, P. P., Bannor, R. K., Prah, S. and Babu, S.** (2024). Towards sustainable food crop production: drivers of shift from crop production to mining activities in Ghana's Arable Lands. *Environmental Challenges*, **14**: p.100835.
- WRB.**1998. World Reference Base for Soil Resources. World Resources Report. No. 84. FAO, Rome.
- Xu, X., Zhao, Y., Sima, J., Zhao, L., Mašek, O. and Cao, X.** (2017). Indispensable role of biochar-inherent mineral constituents in its environmental applications: A review. *Bioresource Technology*, **241**:887-899.
- Yu, H., Zhang, Z., Zhang, Y., Fan, P., Xi, B., Tan, W.** (2021). Metal type and aggregate microenvironment govern the response sequence of speciation transformation of different heavy metals to microplastics in soil. *Science of The Total Environment*. **752**:141956.
- Zhou, X., Lai, C., Almatrafi, E., Liu, S., Yan, H., Qian, S., Li, H., Qin, L., Yi, H., Fu, Y. and Li, L.** (2023). Unveiling the roles of dissolved organic matters derived from different biochar in biochar/persulfate system: mechanism and toxicity. *Science of The Total Environment*, **864**: p161062.