Chapter

The Potential Roles of Biochar in Restoring Heavy-Metal-Polluted Tropical Soils and Plant Growth

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Abstract

Biochar shows interesting and environmentally useful properties, among which is its relatively high cation exchange capacity (CEC). High CEC may lower the easily plant-available heavy metals in soils due to the increase in the soil adsorption capacity resulted from biochar application. Quite a lot of current researches reveal that the extracted heavy metals in tropical soils particularly Cu and Zn were significantly lowered in the presence of biochar at 5–10 Mg ha^{-1}. Heavy metal–contaminated tropical soils planted with corn plants (*Zea mays* L.) show significant decreases in Cu and Zn concentrations at moderate- and high-level addition of heavy metal–containing waste. The growth and dry masses of roots and shoot of corn plant improved immediately as a result of biochar amendment. Planting heavy metal–polluted soils treated with biochar with thorny amaranth (*Amaranthus spinosus*) also demonstrated a similar phenomenon.

Keywords: biochar, heavy metals, tropical soils

1. Introduction

Heavy metal contamination and pollution in soils and environment are still of a serious concern since the presence of heavy metal may directly and indirectly endanger living things [1–12]. Reports on the occurrence of soil contamination and pollution come intensively from all over the world related to modern industries [1–4, 7, 10, 13–31]. The negative effects of heavy metals on plants, animals and human beings are also documented in the current literature [5, 6, 8, 9, 25–26, 30, 32–35]. One important case of the negative effects currently documented was the occurrence of Minamata and Itai-itai diseases in Japan [2]. These suggest that the problem related to heavy metals in the soil environment must be more extensively studied.

Among the various chemical methods available to cope with heavy metal contamination and pollution in soils is the use of organic materials [13, 36–43]. Organic materials such as plant compost may enhance the capability of soil materials to immobilize soil mobile heavy metals. Composted organic matters may effectively lower the soil mobile heavy metals to lower their concentrations to the levels that are not harmful to plants and animals. Organic matters may consist of various functional groups such as phenolic, carboxylic and hydroxyl that may increase the soil cation adsorption capacity [2]. Therefore, the addition of organic matter compost into heavy-metal polluted soils was reported to significantly decrease the soil mobile heavy metals [41, 42]. For example, the addition of cassava (*Manihot utilissima*) leaf compost into tropical soils amended with heavy metals containing waste significantly lowers the soil DTPA extractable Cu and Zn [41]. This phenomenon was observed in the laboratory and greenhouse experiment employing some tropical soils of Alfisols, Ultisols and Oxisols from Lampung, Indonesia. A recent report also showed that the residual Cu and Zn in industrial waste amended soils were lower in soils treated also with cassava-leaf compost [41, 42]. The effect was more significant at sampling time < 10 years amendment [42].

Some researchers [41, 42, 44] reported that the effect of organic matter compost was more significant when added simultaneously with other potential materials. The addition of organic matter compost and lime was shown to better decrease the soil mobile heavy metals [37, 41, 42, 44]. The results of research in [41, 42] showed that the lowering effect on soil heavy metals of cassava-leaf compost and $CaCO_3$ was significantly greater than addition of organic matter or lime alone. The DTPA extracted Cd from Ultisols, Oxisols and Alfisols was significantly lowered by additions of cassava leaf compost and lime [41, 42]. The residual Cu and Zn were also lower in soils amended with cassava-leaf compost and $CaCO_3$ than with organic compost or $CaCO_3$ alone [42]. The presence of increasing OH^- ion by the increase in soil pH [45] may have stimulated the H releases from the organic functional groups and thus widened the capability of the soil materials in adsorbing the heavy metal ions from the soil solution. The adsorption of heavy metal free ions by soil materials may stimulate the releases of heavy metals held as chelates and complexes and also soil heavy metal precipitates and thus finally lower the soil extracted heavy metals.

As shown by numerous data, organic matter compost may significantly affect the soil concentrations of heavy metals. Most reports show that various organic matter may significantly decrease the soil concentrations of heavy metals. However, several reports demonstrated that organic matter may relatively quickly decay in soil system [13, 42, 43, 46]. These observations suggest that the use of organic matters to lower the concentrations of heavy metals in soils is limited for a short duration. Their effectiveness is lower for long-time uses. The problem will be more significant in tropical regions where the soil average temperature and moisture content are relatively high. Therefore, other materials with high durability to organic decomposition are needed. Current literature suggests that biochar will be the best candidate for this purpose [38, 44, 45, 47–62]. As reported by [45, 57], biochar is produced through pyrolysis or charring, causing their structure and composition to be more stable and durable in soil system. In addition, biochar also possesses chemical properties better than ordinary organic materials in terms of cation exchange capacity, pH, specific surface area and nutrient contents.

This chapter was to evaluate the properties and effects of biochar in restoring heavy metal–contaminated or contaminated soils and their effect on the concentration of heavy metals in soils affected by heavy metal–containing materials like industrial wastes.

2. Effects of high concentrations of heavy metals on plant growth

Heavy metals are detrimental to living things, particularly at high concentrations [2]. As mentioned previously, their negative effects are reported from various sites in the world. Research report in [63] shows the negative effect of heavy metal–containing waste on the growth of water spinach, caisim and lettuce in 23 years old heavy metal–containing waste amended tropical soils. Clearly found that the growth of these plants was depressed at high heavy metals and the growth in control soil was the best (**Figure 1**). Lettuce was not survived at high heavy metal contents only until 2 weeks after planting (WAP). It is also obvious that water spinach grew better than the other two plants at any level of soil-heavy metals.

The data above demonstrated that high concentrations of heavy metals (in this case Cu and Zn) were detrimental to plants (**Figure 1**). Their effects are dependent on their concentrations and plant species. Higher concentration of heavy metals gave more significant effects. Water spinach was more adaptable to high concentrations of heavy metal and therefore it grew much better. It is possible to employ plants like water spinach in phytoremediation. Biomass analysis showed also that the plant uptake of Cu and Zn of water spinach was much higher than were other two plants [63].

A similar phenomenon was demonstrated by thorny amaranth. The growth of thorny amaranth was significantly retarded in 24 years old waste amended soils with high heavy metals (treated with 60 Mg waste ha^{-1}) (**Figure 2**). The retardation occurred along the growing time from 0 to 6 WAP. Low heavy metals (treated with 15 Mg waste ha^{-1}) only slightly lowered the growth of this plant.

The effect of heavy metals was more clearly shown by the growth of plant roots. In general, the growth of plant roots may adjust to the high concentrations of Cu and Zn and probably of other heavy metals. This environmental stress by heavy metals may stimulate plant roots to work harder and cause plant biomass to distribute more to plant roots (**Figure 3**). The root/shoot was shown to positively and linearly correlate with the soil-heavy metal concentration. The writer in [64] stated that higher root weight may cause higher root cation exchange capacity (CEC) that may retain

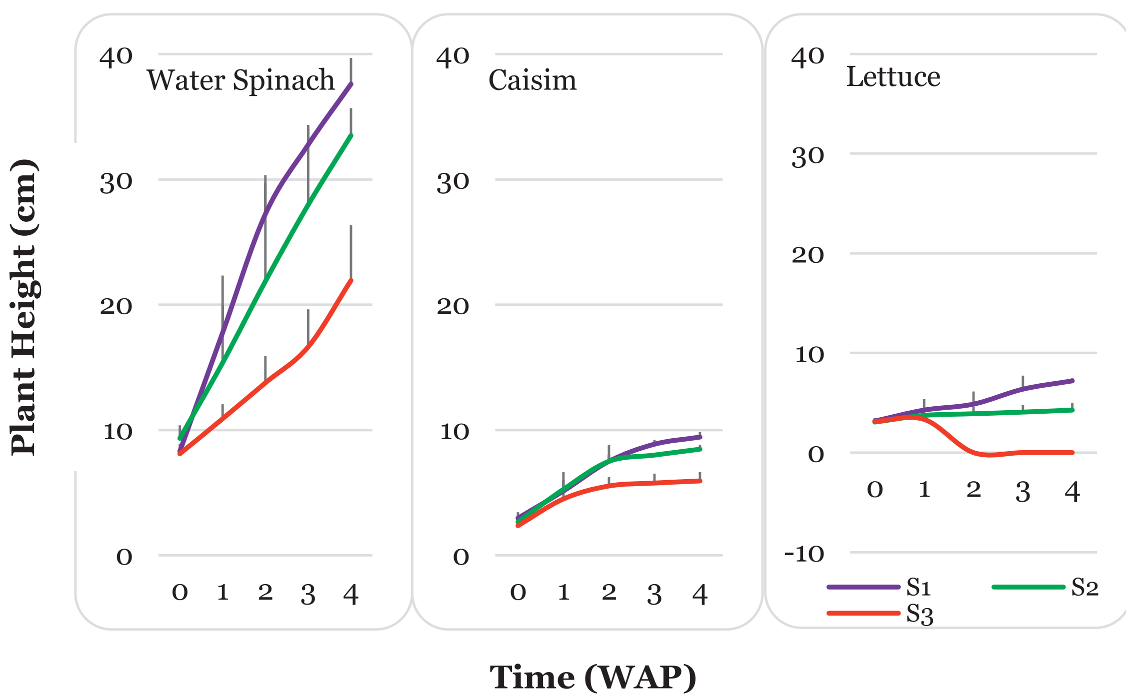

Figure 1.
The growth of several plants in heavy metal contaminated soil (S1 control, S2 low heavy metals, S3 high heavy metals; lettuce dead in S3, WAP weeks after planting) (after [63] with permission).

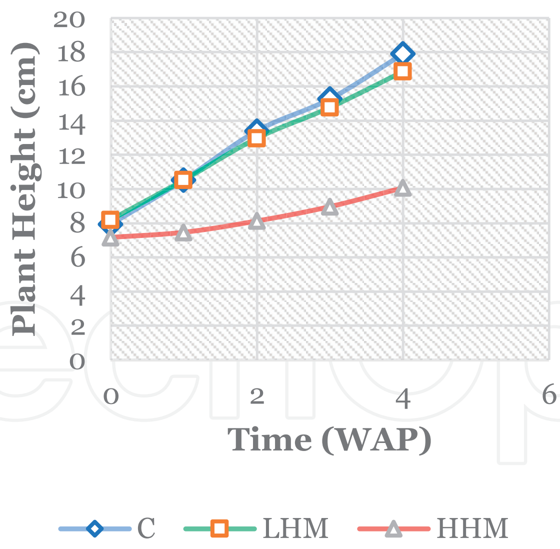

Figure 2.
The growth of thorny amaranth in heavy-metal polluted soils (C control, LHM low heavy metal, HHM high heavy metal, WAP weeks after planting).

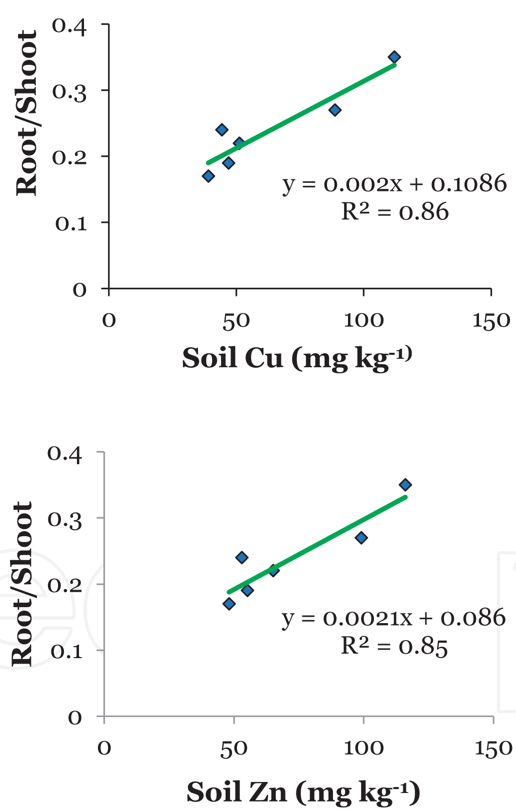

Figure 3.
The relationship between the root/shoot and the soil DTPA extracted Cu and Zn (after [64] with permission).

more heavy metal cations on the surface of plants' roots so that less heavy metals may move to plant shoots. Higher soil CEC may then lower the stimulation of the growth of plant roots. High concentrations of heavy metals in soils caused more biomass distribution to plant roots (**Figure 3**). Higher CEC can be attained by increasing soil pH [2, 65]. Plant roots also produce some exudates such as low molecular organic acids that may chelate heavy metal cations in soil solution and lower heavy metal effects on plants [66, 67].

3. Some physical and chemical properties of biochar

Organic compost is significantly different from biochar both in the process of production and in its properties. Organic compost was produced by a complete decomposition of plant materials in the presence of microorganisms in a well-regulated condition of O_2, heat and water moisture. Urea N is usually added to accelerate the decomposition process while the soil pH is maintained high by lime addition. Microorganism is introduced through cow dung addition. Low C/N ratio is used as a measure of compost maturity. Biochar is produced by incomplete thermo-decomposition of some feedstocks like woods, leaves, feces, straws, husks and manure in a limited or no oxygen supply called pyrolysis or charring [45, 57]. Therefore, biochar consists of much higher C content and consequently, it is more stable with high durability in soils. Reports of [45, 57] show that biochar also showed several better physical and chemical properties. Some of feedstocks abundantly available in Indonesia are woods, straws of corn and rice, bagasse and dairy manure. Therefore, application of biochar may provide a low-cost method of coping with environmental problems. One example of biochar is shown in **Figure 4**, which shows the production of biochar from rice husk and the physical appearance of the rice husk biochar.

Biochar shows porous surfaces so that in the soil system it may physically absorb pollutants like heavy metals. Combined with the increase in the soil adsorption capacity the biochar porosity may significantly enhance the soil retainment on heavy metal cations in biochar-treated soils. In addition to the better physical properties, biochar also shows better, interesting and useful chemical properties [45, 57]. Like organic matters in general, biochar possesses some functional groups like hydroxyl and carboxyl that may bear great amounts of negative charges. It shows a high CEC

Figure 4.
The production of rice husk biochar in the University of Lampung experimental farm (courtesy of Sri Yusnaini with permission).

of 28.8–327 mmol kg^{-1} and high pH depending on the charring temperature, higher at higher charring temperature. The pH of biochar ranges from 5.81–10.1. Biochar also shows high specific surface area (SSA) ranging from 40.99 to 189.8 m^2 g^{-1}.

The potential of biochar at increasing the soil pH may raise the soil adsorption capacity. The increase in OH-ions by biochar treatment may dehydrogenase the biochar functional groups of hydroxyl and carboxyl raising the soil adsorption capacity. Finally, through the synergic works of its high porosity, abundant functional groups and potential to increase the soil pH, biochar may significantly immobilize heavy metal cations in soils.

Therefore, the most important properties of biochar useful in the management of heavy metals in soils is its high SSA, abundant functional groups, high cation exchange capacity and potential to increase the soil pH [45, 57]. Therefore, its presence in heavy metal contaminated or polluted soils may significantly lower heavy metal contaminants. Several mechanisms may involve in the immobilization of heavy metals in soil-biochar mixtures that include physical sorption, ion exchange, chemisorption, complexation and precipitation. Biochar may eventually reduce heavy metal mobility and bioavailability [45]. Wastewater treatment with biochar is reported to immobilize up to 99% of Cd, Pb and Zn in an optimum condition [57]. The effectiveness of biochar is dependent on biomass and soil types and also on heavy metals [60].

4. Improvement of soil chemical properties by biochar

There are several forms of heavy metals in the soil environment [2]. Of which, heavy metal cation is the most directly affected by the active negative charges of soils through adsorption and desorption processes [68–72]. The adsorption of heavy metals that decrease the concentration of heavy metal cations in soil solution may, of course, stimulate the release of heavy metals of other forms such as chelates through de-chelation, complexes through decomplexation, precipitates through dissolution, and other soil chemical reactions that may altogether lower the total concentration of total soil heavy metals as shown in **Figure 5** [2].

The above interrelationship shows the importance of heavy metal cation form in the soil environment and therefore the effort to cope with the problem of heavy metals in soils must be first focused on lowering the concentration of heavy metal cations. The increase in the soil's negative surfaces was repeatedly suggested to suffice this relationship [2]. The presence of soil solid negative surfaces may electrostatically decrease the mobility of heavy metals cations through immobilization process. Heavy metal cations are strongly held by the soil materials and finally decreased the total soil heavy metals in soils as shown in **Figure 6**.

The quantity of heavy metals held by soil materials is negatively charged surface-dependent. High amounts of negative charges are attainable by enrichment with high quantity of negatively charged materials and/or negative charge stimulating materials. Previous observation shows that this condition can be attained by the addition of cassava leaf compost and/or lime materials that were reported to lower the soil concentration of Cd [41]. The cassava leaf compost may provide high amounts of negative charges to its various functional groups. The lime materials may raise the soil pH that may then stimulate the release of H ions from organic matter functional groups. The addition of organic materials and lime material may then finally widen the total negative charges and may increase the immobilization of heavy metal cations in soils.

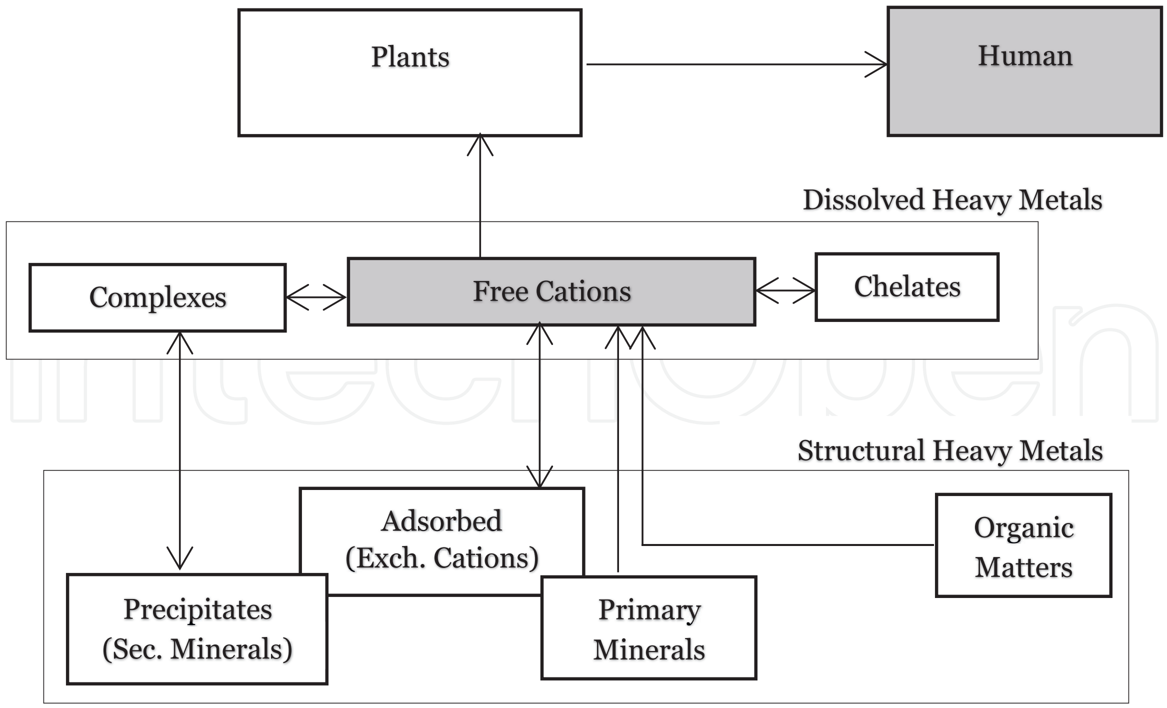

Figure 5.
The interrelationships between various forms of dissolved and structural heavy metals in soils, plants and human (after [2] with permission).

The improvement of the soil negative charges by biochar application may give more significant effect on the amount of the soil negative charges since as stated previously the biochar possesses high amounts of negative charges [57, 59]. The CEC of biochar ranges from 28.8 to 327 mmol kg^{-1} [45, 57]. The increase in soil pH caused by biochar addition may increase the significance of biochar application. Consequently, biochar application may enhance the retainment of soluble heavy metals in soils and finally lower the total extractable heavy metals in soils. This process will provide suitable soluble heavy metal levels in soils and enable plants to grow better.

5. Restoration of heavy metal–polluted soils and plant growth

The relationship between the biochar application, the increase in the soil negative charges, and the improvement of plant growth stated in Section 4 is exemplified in **Figure 6**. The improvement of plant growth by this process is expected in soil contaminated or polluted by heavy metals. Better growth of plants may absorb heavy metals at safe levels and may lower the soil heavy metals from immobilized forms like soil precipitates or soil adsorbed heavy metals much faster. The danger of heavy metals to plants may also be alleviated since plants may absorb heavy metals at lower levels of solubility in the presence of biochar. By this means, the soil's heavy metals are lowered by plants that grow better at safe levels of heavy metals. Thereby plants may also grow better in heavy metal polluted soils.

The decrease in soil Cu and Zn levels in the presence of biochar was currently reported from 23-years old polluted tropical soils planted with corn (*Zea mays* L.) as shown in **Figure 7**. The lowering effect of biochar on the soil extracted Cu and Zn is clearly depicted. The soil concentrations of Cu and Zn decreased in the order of soil treatment with 10 < 5 < 0 Mg biochar ha^{-1}, indicating that the presence of biochar

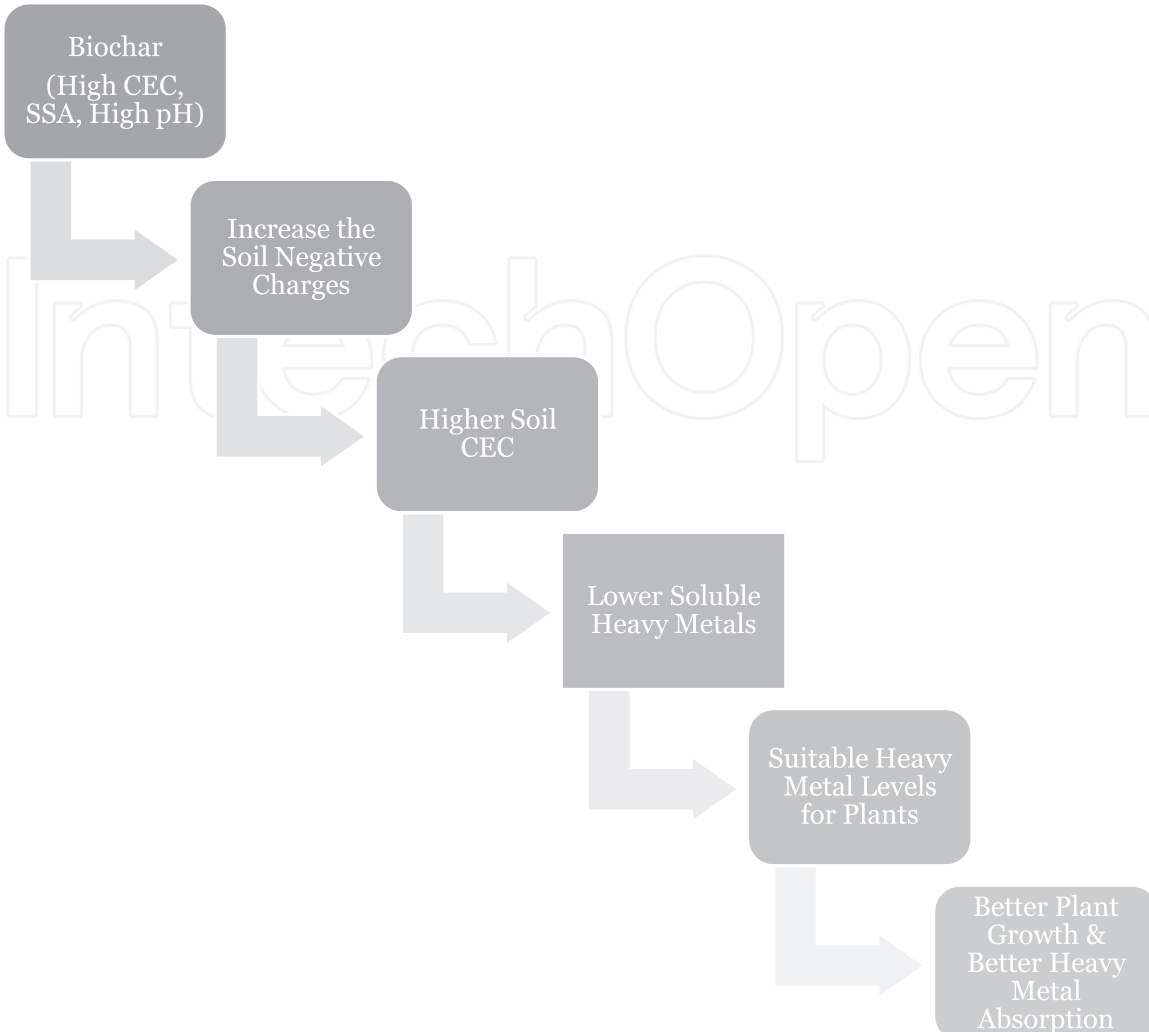

Figure 6.
The effect of biochar application on the soil heavy metal levels and plant growth.

lowered the soil extracted Cu and Zn. The most possible reason for this phenomenon is that the soil adsorption sites for heavy metals were enlarged by the presence of biochar. The enhancement in the soil adsorption capacity towards heavy metals was also probably associated with the significant increase in soil pH by biochar application. This synergic effect of biochar presence in soils may have finally lowered the soil concentrations of Cu and Zn in soils (**Figure 7**).

As the consequence (**Figures 5** and **6**), the growth of corn plants was significantly altered by biochar application, which was indicated by plant height (**Figure 8**) and plant biomasses (**Figure 9**). The trend in the corn plant height was clearly associated with the significant increase in the soil Cu and Zn concentration and the significant decrease in the soil Cu and Zn in the presence of biochar (**Figure 7**). The decrease in plant height was associated with the increase in the levels of amended soils that increase the soil Cu and Zn while the increase in plant height was associated with the decrease in heavy metal concentrations stimulated by the presence of biochar. A similar trend was also indicated by the changes in the plant biomasses as affected by the levels of amended waste and biochar application (**Figure 9**). The corn plant biomasses including corn roots and corn shoots were lowered by soil concentrations of heavy metals and increased in the presence of biochar associated with the decrease in the soil heavy metals (**Figure 9**).

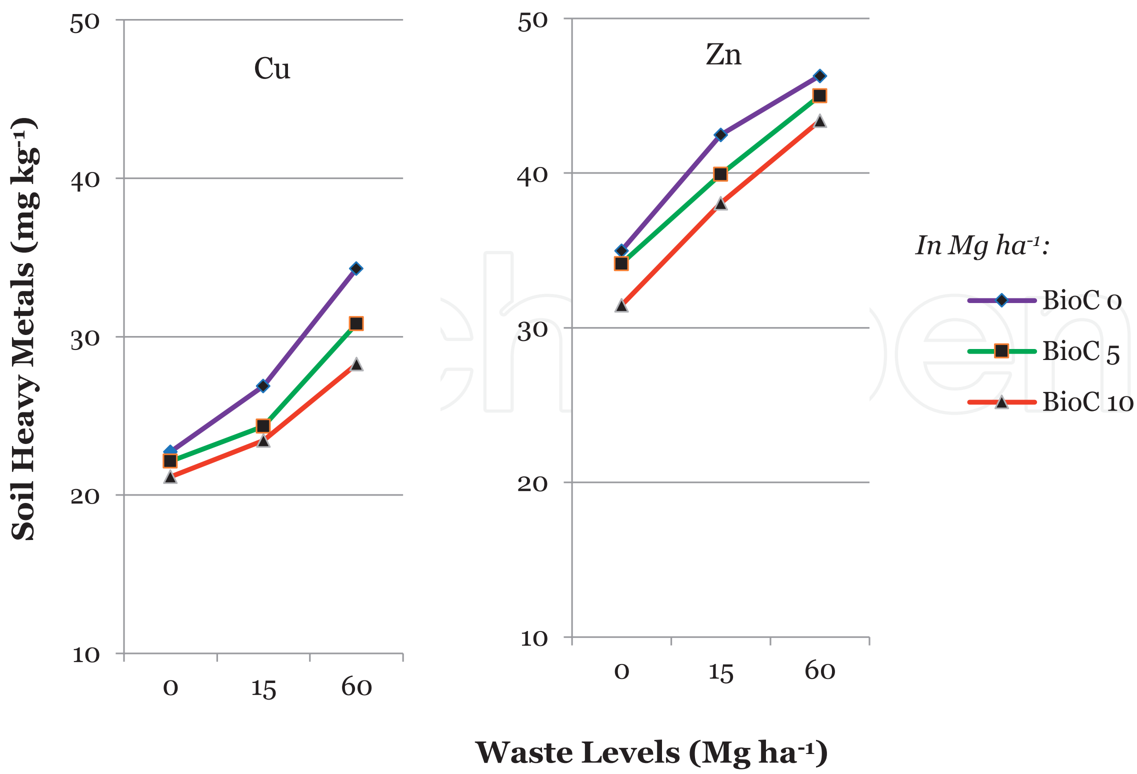

Figure 7.
The effect of biochar on Cu and Zn concentrations in waste-amended soil extracted by N HNO_3 (after [73] with permission).

The research result in [73] showed that the related analysis of variance (ANOVA) also indicated that the amended waste levels significantly enhanced the soil concentrations of heavy metals particularly Cu and Zn and significantly depressed the plant height and plant biomasses (roots, shoots, and the whole plant). Several previous research also showed that the waste-borne Cu and Zn in the soils depressed the growth of several other plants including caisim, corn plant, lettuce, Napier grass, and water spinach [63, 64, 73]. Elevated concentrations of heavy metals in soil system are detrimental to plants. Biochar at 5–10 Mg ha^{-1} was generally effective in changing plant characteristics in heavy metal–containing waste-amended tropical soils. Biochar significantly affected the soil heavy metals, organic C and pH, and also Cu accumulated in corn plant shoots as well as plant height and biomass dry-weight.

The effect of biochar in alleviating the high concentration of heavy metals particularly Cu and Zn was also reported for thorny amaranth [74]. Thorny amaranth was demonstrated to absorb quite high heavy metals from polluted soils and shown to be one of the heavy-metal bio-accumulators and therefore significantly decreased the Cu and Zn concentrations in the 23 years old waste amended tropical soils (**Figure 10**). The presence of thorny amaranth was shown to significantly lower the soil Cu from 79.3 to 60.0 mg kg^{-1} (24.3% decrease) and the soil Zn from 69.2 to 57.4 mg kg^{-1} (17.1% decrease) at the waste level of 60 Mg ha^{-1}. The decreases were much higher or 46.0% for Cu and 24.3% for Zn at lower waste level of 15 Mg ha^{-1}. Copper and Zn showed similar behavior in response to planting but the per cent decrease of Cu was higher than that of Zn, demonstrating that Zn was less mobile and less easily absorbed by plant roots than was Cu. It is stated in [74] that not all lost Cu and Zn was absorbed by plant roots. Some of these heavy metals may have also

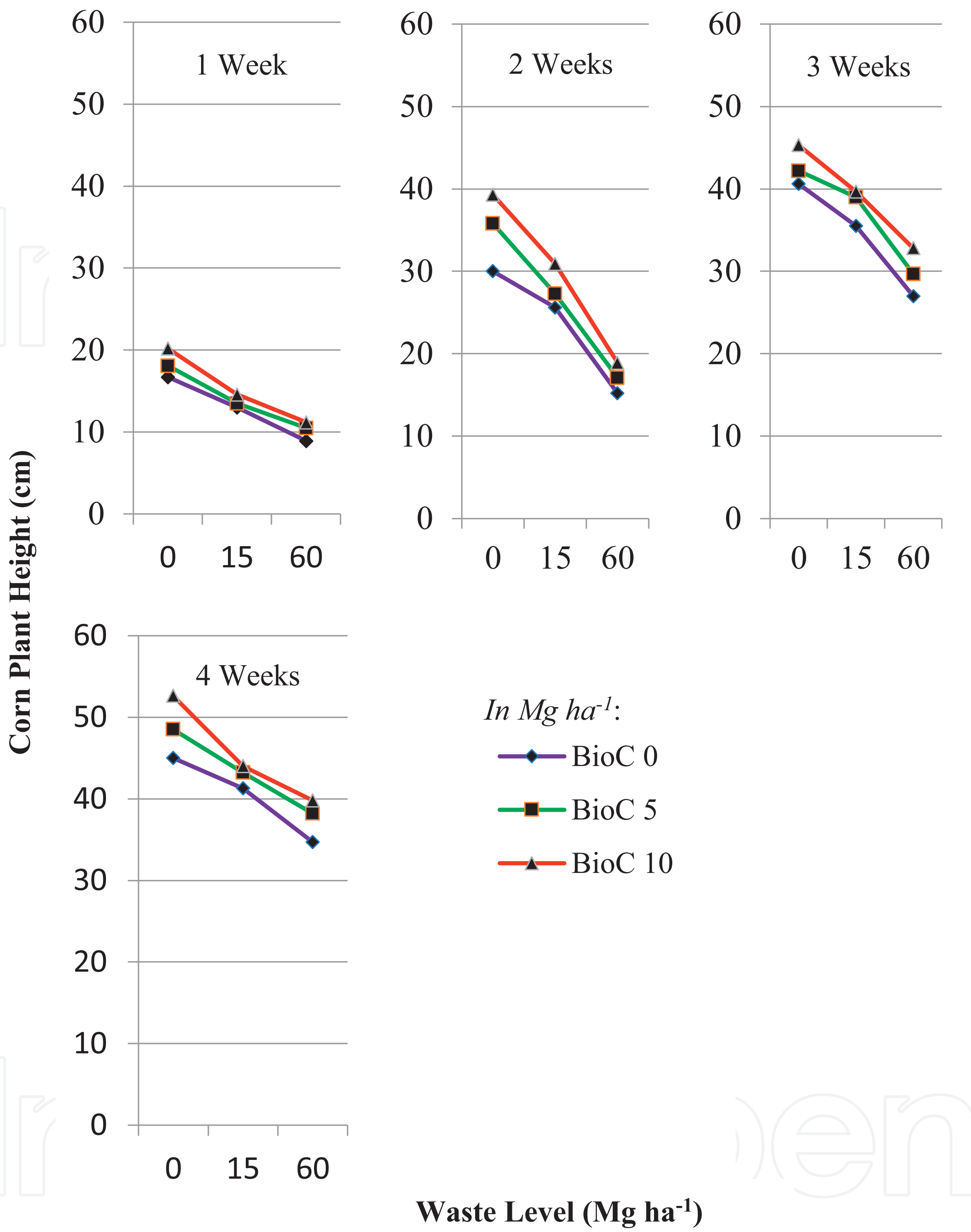

Figure 8.
The improvement of corn plant height in waste-amended soil by biochar (after [73] with permission).

shifted to more strongly adsorbed heavy metals due to the increase in soil pH caused by planting. Copper was probably more easily and strongly adsorbed by soil colloids or precipitated than was Zn.

The lowering of total heavy metals was also expected in phytoremediation. As stated in [75], at suitable levels, the absorption of heavy metals by plant roots may proceed fast enough since the presence of lower levels of heavy metals will not disturb the physics and works of plant roots during phytoremediation. The amount

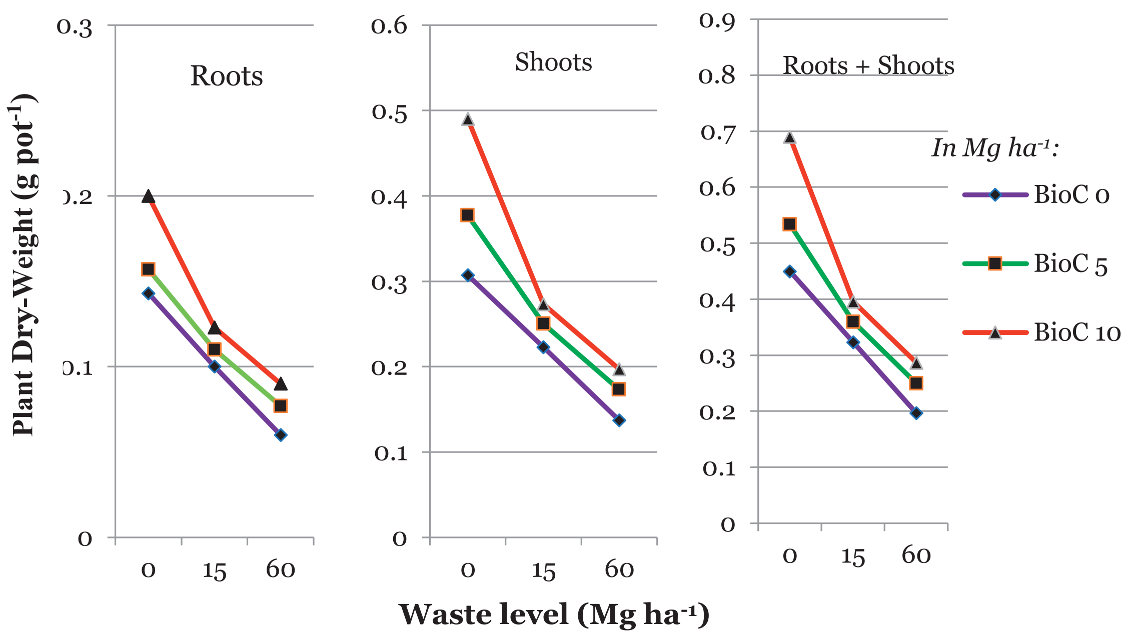

Figure 9.
The improvement of corn plant biomasses in waste-amended soil by biochar (after [73] with permission).

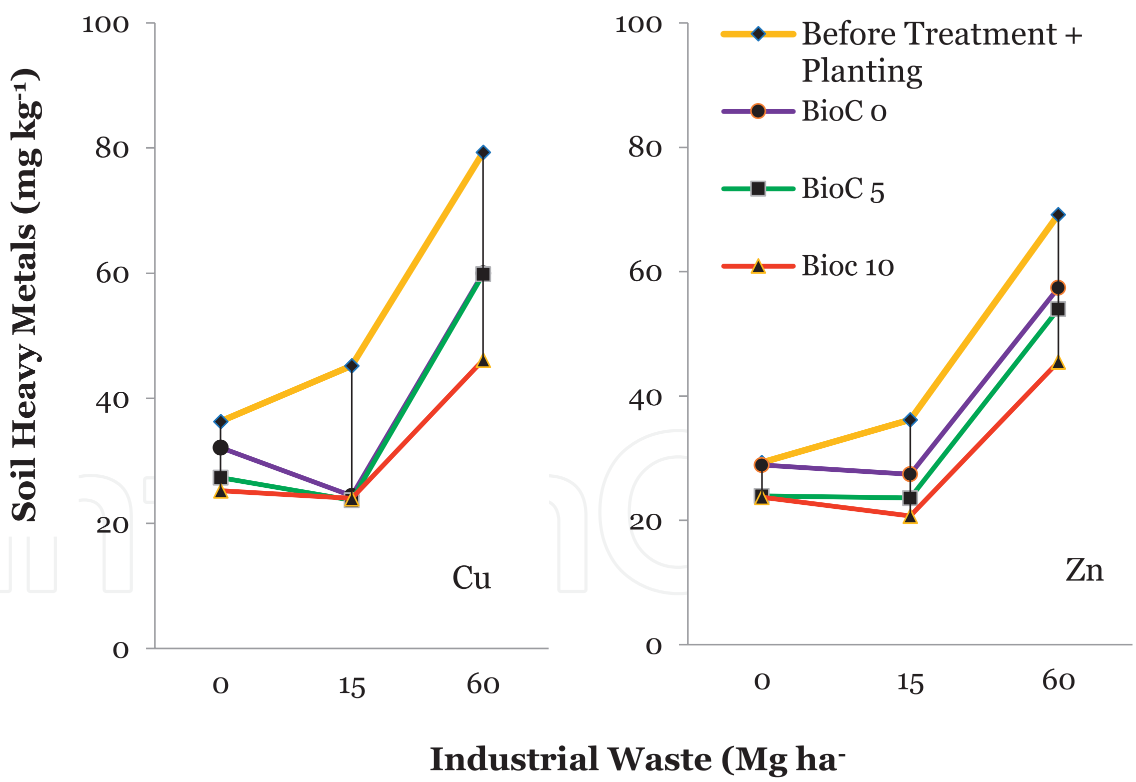

Figure 10.
The effect of thorny amaranth on the concentrations of Cu and Zn in a heavy-metal-polluted tropical soil treated with biochar (after [74] with permission).

of heavy metal removal may be higher at lower than that at higher levels of heavy metals. Therefore, the presence of biochar, which lowers the soil concentrations of heavy metals (**Figure 10**), may fasten the cleaning of heavy metals in soils by phytoremediation.

A similar trend with that in the growth of corn plants was observed in the plant root and shoot dry weights of thorny amaranth (**Figure 11**). The waste origin Cu and Zn may have disturbed the physiological functions in plant tissues and inhibited the growth of plant roots and shoots. It is clearly shown in **Figure 11** that, without biochar, waste treatments lowered the shoot dry weights by about 25.8% and 36.4% at waste treatment of 15 and 60 Mg ha^{-1}, respectively. These values were related to the increase of 8.90 (24.5%) and 43.0 mg kg^{-1} (116%) in Cu or 6.9 (23.5%) and

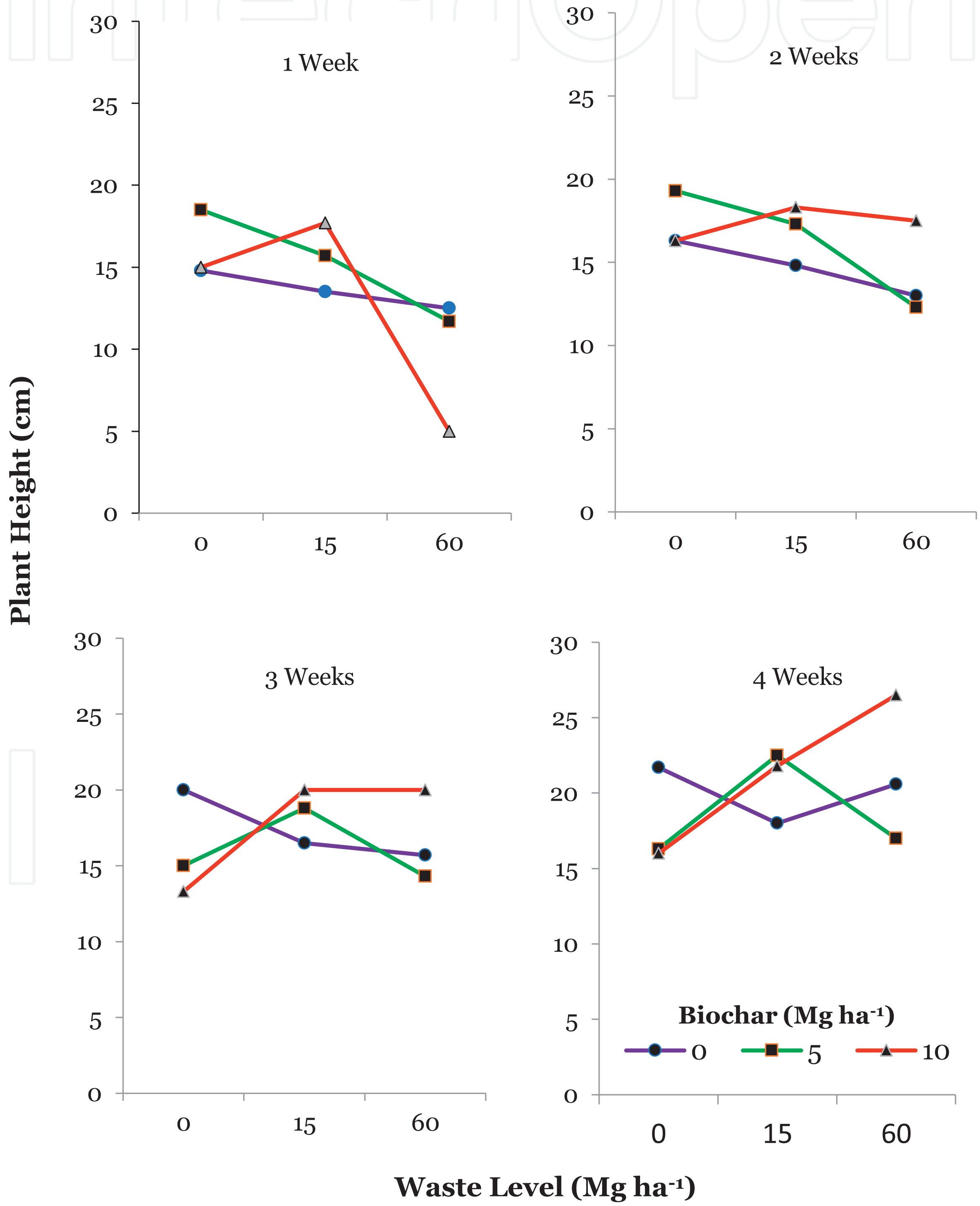

Figure 11.
The growth of thorny amaranth in heavy-metal polluted tropical soil treated with biochar (after [74] with permission).

32.9 mg kg^{-1} (112%) in Zn caused by the respective waste addition. The higher the soil Cu and Zn concentrations the more effective the heavy metal effect on plant shoot growth retardation. A similar trend was observed in the same soil samples for other plant species like caisim (*Brassica chinensis*), lettuce (*Lactuca sativa*), Napier grass (*Pennisetum purpureum*), and water spinach (*Ipomoea aquatica*) [63, 64, 75]. The growth of these plants was significantly retarded by the increase in the soil extracted Cu and/or Zn caused by waste treatment.

The root dry-weight increased by waste addition at 15 Mg ha^{-1} (**Figure 9**), suggesting that the growth of roots was more progressive under high concentrations of Cu, Zn and other heavy metals. This pattern was also reported by [74]. The study in [64] showed high correlation between the root/shoot of Napier grass with the soil concentration of Cu and/or Zn (**Figure 3**). However, high concentrations of heavy metals were found to decrease the root weight of thorny amaranth, suggesting that these plant roots were negatively affected by the higher concentration of Cu and Zn at a waste level of 60 Mg ha^{-1}.

Since it is reported to have high cation exchange capacity and high effect on soil pH [18, 35, 36], biochar was shown to improve the above agronomic responses of thorny amaranth (**Figures 11** and **12**). The presence of biochar may have increased the soil adsorption capacity and lowered the soil labile fractions of Cu and Zn, thereby alleviating their phytotoxicities and finally stimulating the plant growth. Numerous observations demonstrated that high soil Cu and Zn in general decreased with biochar treatment. Calculation shows that the extracted Cu at waste levels of 60 Mg ha^{-1} were 60.0, 59.8 and 46.1 mg kg^{-1} with biochar treatment of 0, 5 and 10 Mg ha^{-1}, respectively, and those for Zn were 57.4, 54.0 and 45.5 mg kg^{-1}, respectively. The increase in the soil adsorption capacity caused by the presence of biochar significantly decreased the soil labile Cu and Zn about 0.33 and 0.59%, respectively, at 5 Mg biochar ha^{-1} and 23.2 and 20.7% at 10 Mg biochar ha^{-1}, respectively. The increase in the soil adsorption capacity towards Cu and Zn was probably to be originated from the unique characteristic of biochar that possessed high amounts of organic functional groups that may provide abundant negative charges. Copper and Zn in biochar-treated soils were transformed into less soluble forms with higher bonding energy. The amount of stabilized heavy metals was determined by the biochar-treated soil-adsorptive surfaces. Therefore, biochar 10 Mg ha^{-1} was more effective than 5 Mg ha^{-1} in decreasing heavy metals at waste level of 60 Mg ha^{-1} (**Figure 10**). These changes may lower the negative effect of heavy metals on the growth of thorny amaranth. Therefore, the treatment of soil with biochar may improve the growth of thorny amaranth in heavy metal polluted soils.

The increase in soil pH induced by biochar treatment may have stimulated the enlargement of the soil adsorptive sites caused by the dissociation of biochar and soil colloid functional groups. However, as pointed out previously, a biochar level of 5 Mg ha^{-1} was probably not sufficient to handle heavy metals at a waste level of 60 Mg ha^{-1}, and the growth of plants at this treatment was in general not better than those without biochar (**Figure 12**). It is obvious that the effect of biochar was dependent on its level. The level of 5 Mg biochar ha^{-1} was effective at a waste level of 15 Mg ha^{-1} but not at a waste level of 60 Mg ha^{-1}. Biochar level of 10 Mg ha^{-1} was effective at waste levels of 15 and 60 Mg ha^{-1}. The improvement effect of biochar was also observed on plant shoot and root dry-weight (**Figure 12**). The improvement of shoot dry weight was clear; the effect of 5 Mg ha^{-1} was more effective than that of 10 Mg ha^{-1} as also that on root dry-weight (**Figure 12**).

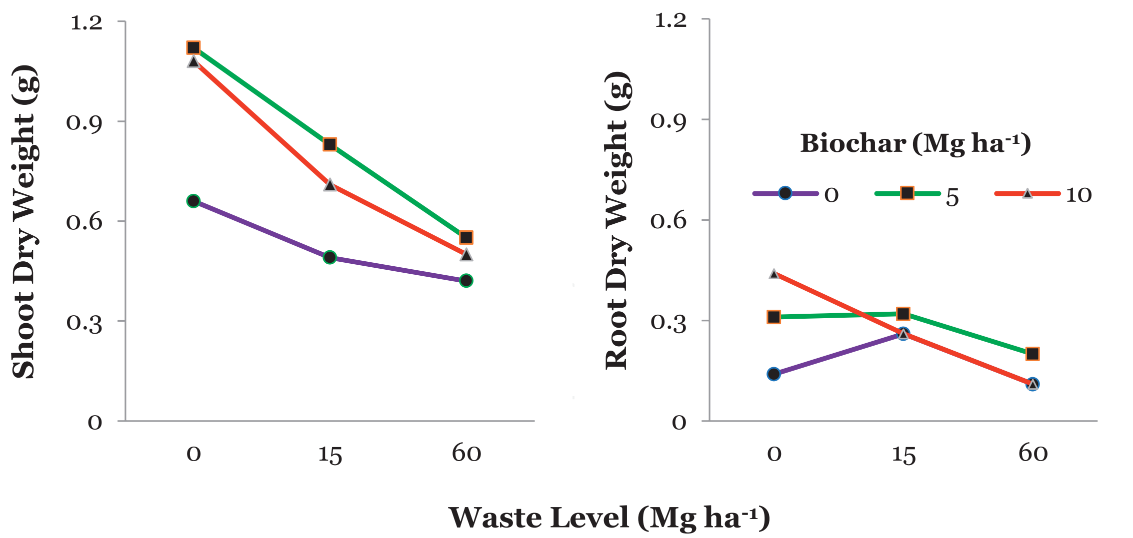

Figure 12.
The effect of biochar on the dry weights of thorny amaranth biomasses in tropical soil polluted with heavy metals (after [74] with permission).

6. Conclusions

The increase in the soil and environmental concentrations of heavy metals are reported from all over the world. The increase in heavy metal concentration may occur stimulated by industrialization. Since they are toxic and detrimental at high concentrations, the increase in the soil's heavy metal concentrations is reported to induce plant growth retardation. The presence of biochar that possesses high amounts of negative charges and may increase the soil pH may enlarge the soil's heavy metal cation retention. Therefore, the biochar application may increase the heavy metal immobilization in soil and cause a decrease in the soil available heavy metals. By these means, biochar application may also increase the growth of plants.

The biochar application may lower the soil concentration to the level at which plants may absorb heavy metals at suitable levels so that the absorption of heavy metals and the decrease of heavy metals in soil occur faster without physical and physiological disturbance. In phytoremediation, the use of biochar may accelerate the heavy metal absorption without physical and physiological disturbance on plant roots by the presence of high concentration of heavy metals.

However, in addition to its advantages to lower the concentrations of the polluting heavy metals in the environment, the use of biochar shows drawbacks, among which is the fact that biochar is bulky. The levels used in most experiments which were 5–10 Mg ha^{-1} are of great amount. It will cause difficulty in its field transportation and treatment. This needs further research to utilize biochar at lower levels without decreasing its effectiveness, for example by adjusting its particle size.

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