

Mitigating Cadmium (Cd) Toxicity in Montane Forest Soils Using Biochar: Laboratory Trial for Soils from Horton Plains, Sri Lanka

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Abstract

Horton Plains (HP), one of the two montane forests in Sri Lanka and habitat to many endemic species of plants and animals, has been severely affected by forest dieback. Past research has identified a direct link between soil pollution with Cadmium (Cd) and the phenomenon of forest dieback. As a consequence, forest dieback is increasing proportionately to the soil pollution. Hence, this study focuses on identifying a cost-effective remediation technique to neutralize soil Cd, and thereby reducing forest dieback. Soil samples were collected from HP, mainly Thotupolakanda site which shows more than 90% severity of forest die back, and bulked together. The soil was high (13.4) in organic matter and low (5.42) in pH, and three soil amendments were tested in this research as; bio char prepared using 1) rubber nut shells, 2) rice husk, and 3) dead wood from HP. Each sample was spiked with 20 ml of 5 ppm (parts per million) Cd solution, and four treatments a) soil + rubber-nut shell biochar (T1), b) soil + rice husk biochar (T2), c) soil + wood-from-HP biochar (T3), and d) soil only (T4), with five (05) replicates, were setup. During the first eight weeks after the application of treatments, it was observed that T1 showed the best performance, by showing a consistent trend in reducing the available soil Cd, with T2 following closely. The interesting observation was that the natural forest soil (T4) was also able to buffer the loading of Cd. At the close of the experiment, it was observed that the available soil Cd goes almost to zero, in less than 24 months.

Keywords

Forest Dieback, Soil Amendments, Cadmium, Biochar, Natural Geosorbents

1. Introduction

Skeletons of dead and dying large trees have become a common feature of most of the area in Horton Plains (HP), Sri Lanka. Untimely death of trees and large scale destruction of the natural montane forest vegetation appears to have brought a massive destruction to this important natural resource. Multiple tree death in this montane forest, where the trees normally lose their foliage from top to bottom, without showing any clear sign of a physical disturbance, insect attack, orfungal disease-i.e. Forest dieback in the HP, was first observed in Thotupolakanda and reported by Perera [1]. Ranasinghe et al. [2] and Chandrajith and Dissanayake [3] have precisely identified two of the key causes for the destructive forest die-back in HP-i.e. Cadmium (Cd) and Lead (Pb) in the forest soil. Through the interference with respiration and other crucial metabolic functions of the forest vegetation, death is inflicted to the plants by these toxic heavy metals [4]. Of the many heavy metals, Cd is one of the most mobile, and is therefore highly bio-available, and yet, the mobility is controlled by soil characteristics like pH, texture, and the organic matter content [5]. The accumulation of Cd and Pb in the soil at toxic levels is mostly due to anthropogenic activities like agricultural, mining and industrial activities. As a result, a number of countries have come up with national norms regarding the permitted levels of various toxic elements in the soil matrix. Levels of concentration, depending on the soil pH, are termed as: 1) Reference level, 2) Research level, and 3) Priority intervention level. The reference level for agricultural soils is 90% of the heavy metal concentration of natural, non-polluted soils. This is also the highest value permitted for non-polluted soils. The research level must be applied to anything above this level, and when a soil is considered to be polluted, the potential toxicity should be determined after subjecting it to various determinations, which are chemical in nature, as biological evaluations have not been recommended. The highest level of toxicity, the intervention level, indicates levels that are considered dangerous to soil, which needs priority remediation [6].

A major factor of the dynamic soil quality (soil health) is determined by natural soil microbes, whose activities will be degraded through the toxicity of these two metals. Additionally to this, the overall quality of the water is determined by the health of the soil. HP is much more than a natural forest. It is the most important water catchment in the island of Sri Lanka, feeding three (03) major rivers—Mahaweli, Walawe, Kelani [7]. As such, there is an urgent need to find a practical and sustainable method to contain, and then cleanse the heavy metal contamination of soils. The reason behind this is, elements like Cd and Pb are considered to be nonessential metals to plants, on the contrary, toxic [8] [9] to plants, thereby negatively impacting the soil health, and consequently degrading the quality of the water in Sri Lanka linked to the catchment of HP. Under the classification, HP is an Upper Montane forest, and upper montane vegetation overreacts even to minor changes in the environment [10]. Thus, healthy existence of this precious resource will be crucial for the sustenance of the bio-diversity, water supply, agriculture, food security and the livelihood of the majority of the population in Sri Lanka. Additionally, HP is a significant tourist attraction that generates an immense income to the country's economy. HP is also a special natural habitat for some extremely rare species of flora and fauna.

One of the isolated key contaminants, Cd, can neither be destroyed nor removed via ordinary chemical or biological remediation techniques. Therefore, the only option left will be to utilize an *in-situ* method to effectively immobilize these elements. Through this, the movement and the impact of this contaminant within the forest eco-system could be successfully restricted. Provided that the right immobilizing agent—*i.e.* geo-sorbent—is used, the detoxification will be permanent. Since the HP is a protected, extra-sensitive natural eco-system, the remediation techniques to be introduced must not interfere with natural functioning of the system, and as such, the use of a natural geo-sorbent, such as biochar, is one of the best options.

The thermal degradation of organic materials without oxygen, or with minimal concentration of oxygen (pyrolysis) results in a solid product, "char". It is coined as "biochar" when utilized as a soil amendment to improve fertility and sequester carbon (C) [11]. Per the temperature that is selected during the pyrolysis process, and with the feedstock type, the amount of existing carbon in biochar will vary [12] [13]. For example, the net C mineralization and N₂O emissions from sandy and silt-clay soils amended with poultry litter biochar at 400°C were significantly greater than when compared with biochar from swine manure [14]. One of the major characteristics shown by biochar is its' high stability against decay, while the other is having a higher ability to retain nutrients when compared to other forms of soil organic matter. Hence, biochar is ideal for use as a soil amendment, benefitting the environment in different ways such as; 1) mitigation of climate change, 2) improvement of soils, and 3) reduction of environmental pollution [11]. However, the stability of any biochar depends on many factors, for example, nature of the reactions between the biochar and soil constituents like dissolved organic and inorganic matter, microbes, and plant roots.

A number of studies have demonstrated the high capacity of biochar to adsorb pollutants in soils [15] [16] [17] [18]. A major factor contributing to the sorption of contaminants is the physical structure of the biochar. This is because the surface area increases by some thousand-fold during the pyrolysis process, when compared to the original material. This in turn provides a large number of sites for sorption [16] [17]. Using carbon containing materials such as activated carbon, black carbon, and biochars for mitigating metal toxicity via trapping, and as a soil conditioner to facilitate plant performance is increasing, due to their high surface area and reactivity. When it comes to carbon sequestrating and soil conditioning, black carbon, biochar, and other conventional charcoals show many similarities. Yet, in most cases, they would act differently when used for adsorbing heavy metals. Based on the pyrolysis parameters such as the oxygen content and combustion temperature, and the sources of biomass used for biochar production, the sorption capacities will show significant differences [19].

Cd, which is non-essential to plants, is recognized as a metal contaminant. Therefore, it can also be considered as a major environmental concern as its prevailing time in soil is more than a thousand years [20]. Several changes to the biochemistry, physiology, and structure of plants in the soil-plant relationship can be observed due to the presence of Cd. Additionally, Cd toxicity could result from disturbance in plant metabolism, as a consequence of disturbance in the uptake and translocation of mineral nutrients [21]. Researchers have also shown that Cd toxicity can reduce both photosynthesis and the mineral nutrition in plants [22] [23] [24]. Additionally, observations have shown that Cd induces oxidative stress in plants via increasing the production of reactive oxygen species [25], which could potentially damage the biological macromolecules and create chaos in the antioxidant system in plants.

Researchers have worked on investigating the efficacy of using biochar to immobilize the heavy metal Cd in soil [26]-[31]. For example, in a heavily contaminated soil with biochar added to it, an 87% uptake of the heavy metal Cd, in comparison to the Cd uptake of the barley that grew in the same soil with no biochar, was observed. This further revealed that the plants' uptake of heavy metals was substantially reduced in soil which contained 2% biochar [32]. The capacity of immobilizing Cd²⁺ ions from a heavy metal contaminated soil in Sri Lanka (Entisols) mixed with coconut shell biochar have been shown to be above 80% [31]. The chemical constituents of biochar reveals the presence of myriads of active sites, which could form strong bonding with positively or negatively charged toxic metal ions [33]. Additionally, the sorption capacity of metals decreases increasing acidity [34] [35] [36].

Biochar has tightly packed aromatic structures, for enabling it to exist for longer periods of time without getting degraded by microbes, as shown in anthrosol soils in which biochar was applied as a soil remediating agent [37] [38]. The older the biochar, the higher its efficiency is, to immobilize heavy metals and metaloids. This is because oxidation of biochar continues through aging, results a higher number of carboxyl groups. It means that the total minus charge increases, leading to an increase in cation exchange capacity [39]. Consequently, the persistent impact of biochar on immobilizing toxic metals depends on its existence in soil, and there is also an increment in charge with time. Metal trapping efficiency of biochar is affected by the variations in soil reactions that influence the pH induced ionic nature [40], the pyrolysis temperature, and raw materials that impact the availability of active groups that generate metal complexes [41]. Additionally, neutralization of toxic metals is linked with the amount of minerals in the related ash in most biochar products (e.g. phosphate) [42], and through the variations in the surface area and porous nature of biochar [43]. These characteristics are determined through the raw material used, the pyrolysis temperature, and the production conditions such as residence time and heating rate [44] [45]. The effectiveness of specific biochar materials also depends on soil properties [46], the particular heavy metals of interest [47], and the variations between plant species with their nature of root growth, and their capabilities to adsorb and store heavy metals [48].

However, the use of biochar as an in-situ remedial measure for montane forests with severe dieback is yet to be investigated in detail. As such, this study is a preliminary laboratory trial to assess the efficacy of using biochar as a cleanser for forest soils contaminated with Cd.

2. Materials and Methods

2.1. Study Area

The soil samples for the experiment were collected from Horton Plains, Sri Lanka (as shown in **Figure 1**), an identical tropical montane forest between the altitudes of 1500 and 2524 m above MSL [49]. Geographical location of Horton Plains is about 32 km south of Nuwara Eliya in the Central Highlands of Central Province, with latitudes between 6°47"N and 6°50"N, and longitudes between 80°46"E and 80°50"E [50].



Figure 1. Locations of soil samples used in the bulking process, in Horton Plains, Sri Lanka.

2.2. Methodology

2.2.1. Characteristic Analysis of Soil and Biochar

The homogenized soil sample for the laboratory trial was prepared by bulking all soils collected from HP. The soil was ground using a mortar and pestle, then sieved through a nylon sieve to 2 mm and air dried at 30°C. The resulting dried 2 mm sieved soil was used for the laboratory studies. A portion of this sample was used to measure basic soil physical characteristics for pH (H₂O) [51], texture [52], EC (Electrical Conductivity) [53] and SOM (Soil Organic Matter) [54] using standard analytical procedures. Extractable Cd was determined by batch methods using the following reagents: 1) de-mineralised water, 2) 0.01 M CaCl₂ [55], 3) 0.05 M CaCl₂ [56], 4) IN Ammonium acetate-acetic acid solution buffered at pH 7.0 [57], and 5) 0.05 M Na₂EDTA [57]. The initial moisture factor of the samples was also measured.

2.2.2. Experimental Setup

Biochar was prepared using three (03) types of raw materials; 1) rubber-nut shell, 2) rice husk, and 3) dead wood from HP, under 400° C - 500° C pyrolysis temperature. The pH, EC, and available Cd concentration were measured for all biochar.

From the bulked sample, twenty (20) separate samples each weighing 25 g, were prepared. Addition of biochar to the soil was 5% by weight. Each sample was then spiked with 20 ml of 5 ppm (parts per million) Cd solution. Four (04) treatments 1) soil + rubber-nut shell biochar (T1), 2) soil + rice husk biochar (T2), 3) soil + wood-from-HP biochar (T3), and 4) soil only (T4), with five (05) replicates, were setup in accordance with the Complete Randomized Design (CRD) (SAS Institute Inc., 2012).

The prepared soil samples were initially incubated for two (02) weeks, and a soil extraction was taken as follows. 4 g of soil was measured into conical flasks and 10 ml of 1 M NH_4NO_3 solution was added into each flask, and sealed with para films.

These were then placed on a shaker and shaken for 3 hours at 180 rpm. Afterwards, all solutions were double filtered through Whatmann No.1 filter papers into test tubes. These samples were analyzed for available Cd concentration using the AAS.

3. Results and Discussion

General characteristics of soil in the study area (**Table 1**) indicate that the soil is strongly acidic [58] and the soil organic matter (SOM) level, 13.2% is high [59].

Organic matter is a key to soil quality, linked with the ecological importance of the soil, which determines ecosystem productivity, affecting climate quality. The critical limit for organic matter in farm soil is 2% by weight, below which the sustainability of soil quality cannot be maintained. The critical limit of organic matter for forest soils is yet to be assessed. Organic matter content of normal forest soils varies between 1% - 5% by weight [59]. Obviously, the cation

Soil texture	Sandy Loam	
pH	5.42	
Soil Organic Matter (SOM)	13.4	
Electrical Conductivity (EC)	4260 µS/cm	
Cation Exchange Capacity (CEC)	210 cmol/kg of soil	

Table 1. General characteristics of the soil sample from HP, Sri Lanka.

exchange capacity (CEC), 210 cmol/ kg of soil, is very high due to the richness of the soil with SOM. Electrical conductivity of 4260 μ S/cm indicates that the soil is slightly saline [60]. Low pH in HP soils is linked with the presence of organic acids with low pKa-values, which are released into the soil solution during the organic matter degradation and by root secretions [61]. Perhaps, the vegetation and litter fall are sources of acidity in soils in HP [62]. Additionally, the area of HP receives a very high rainfall exceeding 3500 mm/year, which is acidic in general, as a result of the formation of carbonic acid from carbon dioxide in the air.

This weak acid results in the pH of the rain to stay 5.0 - 5.5. If the acidity of rain water goes below normal levels, it results in speedy acidification of soil, and when the annual precipitation exceeds 800 mm, the soil pH usually remains acidic [63]. Washing out of alkaline cations (e.g., Na⁺, K⁺, Ca²⁺, and Mg²⁺) present in the soil profile increases soil acidity [64], and severe leaching losses can be expected in HP with the amount of usual rainfall in the area.

A dramatic decline of available form of Cd was observed during the first three weeks after spiking the soil with Cd (as shown in **Figure 2**) in all the treatments including control—*i.e.*, Cd sorption in the soils has continued roughly until the end of the third week from spiking. If observed closely, it can be seen that T1 showed the best performance, by showing a consistent trend in reducing the available soil Cd, with T2 following closely.

One reason for this could be that the rubber-nut shell is high in lignin [65]. Biochar made from heavily lignified materials has been found to be effective in immobilizing heavy metals [66]. The decline of available soil Cd in control indicates that soil itself has a limited but significant capacity to sorb soluble or plant available form of Cd in the soil. However, further studies are needed to understand the extent of the buffering capacity of the soil. But it is helpful to keep in mind that under natural conditions, there is only so much that the soil can safeguard, before the equilibrium snaps and give rise to various issues like forest dieback.

Cd that enters to the soil through different mechanisms is subjected to a myriad of reactions such getting adsorbed on to soil colloids, precipitation, and combining with chemical substances in soil solutions, and consequent adsorption of such combinations to soil fragments. Cd adsorption in soils can be categorized into 1) nonspecific sorption, 2) specific sorption, 3) inorganic or organic ligand mediated sorption, and 4) precipitation or co-precipitation. Under



◆ T1 ■ T2 ▲ T3 × T4 ----- Poly. (T1) ---- Poly. (T2) ---- Poly. (T3) — Poly. (T4)

Figure 2. Fluctuations of soil available Cd (in ppm) during the initial 8 weeks after spiking. The four treatments are; 1) soil + rubber-nut shell biochar (T1), 2) soil + rice husk biochar (T2), 3) soil + wood-from-HP biochar (T3), and 4) soil only (T4).

nonselective adsorption, Cd stays on negatively charged sites on soil colloids via electrostatic bonding. The adsorbed Cd is then assumed to be completely hydrated [67], and can be found in the diffuse double layer as outer sphere surface complexes [68]. The Cd adsorbed nonspecifically is subjected to exchanging ions with different cations present in the soil solution, and is hence assumed as available. This Cd shows vulnerability to be washed out, and exist in a form toxic to biological organisms. The adsorbed Cd is considered to be partially hydrated, and freely exchangable with other adsorbing ions like Zn. For these reasons, presumably, the observed desorption after the third week is a result of other ions which tend to exchange sorbed Cd.

Depending on the constituents of the soil, there are different sites for Cd sorption. Cd is adsorbed electrostatistically on the pH-independent negatively charged sites in the 1:1 and 2:1 layer silicate minerals, and particularly on differently charged sites on alumina faces and aluminol edges [69] [70]. Soil organic matter adsorbs Cd at the negatively charged carboxylic and phenolic groups or directly with these and other active groups, forming monodentate or multidentate bonding. Cd adsorption in soils is impacted by both the solution and solid phases [71].

Soil reaction, or pH, is one of the prominent factors affecting Cd adsorption in soils [72] [73]. Cd adsorption goes up with pH, mimicking a sigmoid-type pattern. It means that the soil acidity in the study area should promote the desorption of Cd to result in an increased toxicity on plants.

However, the addition of biochar may counter the influence of soil acidity on increased desorption by two ways—*i.e.*, neutralizing soil pH, and providing adsorption sites.

To obtain an understanding of the behavior of Cd sorption by the natural geosorbents, a 3rd order polynomial function was fitted to the observations during the first eight weeks of adding the treatments to the soil samples, as shown in **Table 2**.

The immobilization technique used in this study was treating the soil with natural geosorbants—they were biochar produced from different raw materials, expecting the stabilization of mobilized or plant available forms of Cd in the soil, given that the main focus was to reduce Cd mobility and toxicity in soils. It appears that all the biochar types have been effective in immobilizing soil Cd. Biochar has become popular across the world as a remediating agent to neutralize toxic heavy metals in soil and water.

Most biochars are alkaline in nature, and add P, K, and Ca in available forms, which contribute to heavy metal immobilization in soil. It has been proven that the concentrations of Cd and Zn in the leachate can be reduced by 300- and 45-fold, respectively, by the addition of biochar [17]. An important method to retain of Cd and other toxic metallic elements by biochars is the sorption. Application of only 5% to the soil, biochar has proven to be capable of immobilizing 30 - 94 of the available forms of Cd [74].

However, the interactions between different species of ions in contaminated soils may results mobilization of some immobilized ions after the addition of biochar. For example, mobilization of As and Cu has been observed in an experiment after amending the soil with wood biochar [75]. Immobilizing amendments used may have altered the original metal form—*i.e.* toxic fractions for biological organisms to non-toxic, immobilized forms such as immobilized metallic elements or precipitates, via the joint methods of adsorption, complexation, and precipitation. However, T4, the control, also has shown some potential for cleaning itself through the immobilization of soil Cd. The soil is extraordinarily rich with organic matter (13.4%). Soil organic matter (SOM) contains humic substances (humic acids, fulvic acids and humins), and of these, both humic

 Table 2. Best-fit 3rd order polynomial equation—initial 8 weeks after spiking—fluctuation in available soil Cd with the addition of natural geosorbents.

Treatment ID	Treatment Name	Best-fit Equation	Correlation coefficient (R ²)
T1	Rubber Nut Shell	-9E-05x ³ + 11.175x ² - 482725x + 7E+09	0.9881
T2	Rice Husk	$-8E - 05x^3 + 10.368x^2 - 447892x + 6E + 09$	0.9893
T3	HP wood	$-9E - 05x^3 + 11.551x^2 - 498975x + 7E + 09$	1.0000
T4	Control	$-7E - 05x^3 + 9.1344x^2 - 394582x + 6E + 09$	0.9224

acids, fulvic acids also are effective metal immobilizing agents. Organic soil amendments have been widely used to immobilize heavy metals in contaminated environments. Humic and fulvic acids change speciation of metal ions from readily available forms for biological organisms to more-or-less stable and less toxic fractions linked to SOM, metal oxides, or carbonates [76]. Very specifically, the humic acids can make bonds with a range of heavy metals and metaloids such as Cd, Cr, Cu, and Pb [76] [77].

Due to various national and university-level interruptions and constraints, the researchers were unable to measure the available Cd concentration in the soil samples continuously. As such, the next round of samples was measured after a hiatus of 19 months.

It is observed from **Figure 3** that the soil available Cd (in ppm) is very close to zero, with the maximum concentration at 0.01 ppm.

A 3rd order polynomial was fitted (as shown in Table 3) to the observations



Fluctuations of Soil Available Cd vs. Time Final Six (06) Weeks

Figure 3. Fluctuations of soil available Cd (in ppm) during the final six weeks after spiking. The four treatments are; 1) soil + rubber-nut shell biochar (T1), 2) soil + rice husk biochar (T2), 3) soil + wood-from-HP biochar (T3), and 4) soil only (T4).

 Table 3. Best-fit 3rd order polynomial equation—final 6 weeks after spiking—fluctuation in available soil Cd with the addition of natural geosorbents.

Treatment ID	Treatment Name	Best-fit Equation	Correlation coefficient (R ²)
T1	Rubber Nut Shell	$4E-06x^2-0.3624x+7942.9$	1
T2	Rice Husk	$1E-05x^2 - 1.0852x + 23783$	1
Т3	HP wood	$2E-05x^2 - 1.6786x + 36785$	1
T4	Control	$2E - 05x^2 - 1.3724x + 30076$	1

for better understanding and prediction of the behavior of the soil available Cd after 18 months of application. The long-term behavior of biochar in a contaminated soil was observed to have come to equilibrium, close to zero availability.

4. Conclusions

The study in general, has focused on assessing the capacity of natural geosorbants in reducing the bioavailability of soil Cd. It has been observed that the bioavailability goes down, almost to zero, in less than 24 months. Nevertheless, certain key characteristics must be considered when choosing a matching geosorbant for any practical use. The bond between the detoxifying material, the specific metal, and the dominant soil characteristics, should be considered first because, it will principally decide both the detoxifying efficiency and the environmental impacts throughout. Then, before the application of geosorbant in the field, the cost-effectiveness should be evaluated to estimate the general affordability of the techniques. At the same time, natural residue cleansing agents are usually comparatively more cost effective than synthetic agents. Cost is a major contributing factor to the implementation of these natural agents as cleansers, together with detoxifying efficacy of the material. As the principal objective is to use soil remediating agents to mitigate Cd toxicity, the use of geosorbants contaminated with harmful and unwanted elements and compounds, for example other toxic metals and metalloids, toxic organic residues, salts, and radioactive materials above the safety limits must be restricted. In other words, before using, the cleansing agents have to be analyzed for its constituents. Lastly, after using a cleansing material, constant continous observation is mandatory for understanding the detoxification efficacy, connected to other harmful and unwanted materials leaching or increasing the mobilization of toxic metals, plant nutrients, or salts.

At this time, the key limitation of this in-situ soil Cd detoxification technique is that Cd is not taken out from the soil and therefore, persists in the ecosystem as an oncoming threat, simply waiting for activation through unpredicted fluctuations in soil chemical and chemical properties. The challenge is to identify an affordable and practical amendment technique, which is ecologically safe, and is able to concurrently impact multiple contaminants in the long-term. Identifying cost-effective and ecologically sound soil detoxifying agents to fulfill the need for correcting the soil contamination issues in forests and agro-ecosystems in particular, is a timely requirement.

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Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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