

Article

Cocoa and Coffee By-Products for Cadmium Remediation: An Approach to Sustainable Cocoa Cultivation in Colombian Soils

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Abstract

For the successful commercialization of cocoa in the global market, ensuring product quality and compliance with regulations—such as EU regulation, which established maximum cadmium (Cd) levels for cocoa products—is essential. Moreover, cocoa cultivation in Colombian soils, an alternative to coca cultivation, is in many cases an unsustainable practice due to soil degradation, which is accompanied by a drastic decrease in soil organic carbon content. This study evaluated the use of a nature-based solution for cadmium remediation in cocoa cultivation soils by applying three organic amendments: biochar derived from cocoa pod shells (Cocoachar), spent coffee grounds (SCGs), and SCG-derived biochar (SCGchar). The effects of these organic amendments, applied at rates of 5, 10, and 15% (*w/w*), were evaluated in an in vitro incubation experiment (climate chamber) using soil samples collected from Zulia (mountain soils) and Tibú (alluvial soils), located in the Catatumbo region of Norte de Santander (Colombia). Soil analyses included available Cd concentrations (by atomic absorption spectroscopy), physicochemical properties (pH, organic matter, electrical conductivity), and other mineral elements. The results showed that Cocoachar significantly reduced Cd concentrations while enhancing soil quality, particularly by increasing pH and improving soil organic matter content. The application of 15% Cocoachar reduced Cd levels from 0.056 to 0.012 mg kg^{−1} and increased soil pH from 6.3 to 7.0 in Zulia. In Tibú, the addition of 15% Cocoachar lowered Cd levels from 0.12 to 0.05 mg kg^{−1} and raised the pH from 5.0 to 6.1. SCGchar primarily enhanced soil organic carbon, increasing its content from 1.87% to 2.35% in Zulia and from 0.66% to 1.53% in Tibú, thereby supporting ecological balance and sustainable soil fertility. Overall, the recycling of cocoa and coffee by-products into biochar offers a solution within the circular economy and a sustainable way to cultivate cocoa. This in vitro exploratory study must be confirmed with field trials and Cd analyses in cocoa beans.

Keywords: biochar; organic amendment; waste reuse; circular economy; ecofriendly agriculture; responsible management



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1. Introduction

Cocoa (*Theobroma cacao* L.) is a tropical plant whose fruit is an elliptical berry (pod) of a yellow, red, purple, or dark brown color, with seeds called cocoa beans once fermented, cleaned, and dried [1]. A report from the Federation of Cocoa Growers of Colombia (Fedecacao) indicated that in Colombia, a new record in cocoa production was reached in 2021 (69,040 tons), representing an 8.9% increase compared to 2020 [2]. During the 2019–2020 cocoa year, according to the International Cocoa Organization (ICCO), Colombia ranked tenth in global cocoa production and fifth in Latin America [3].

Health legislation, particularly in Europe, encouraged cocoa producers worldwide to focus their efforts on improving bean quality and safety, especially by reducing heavy metal content [4]. EU Regulation (Commission Regulation EU 2021/1323 [5]) established maximum permitted levels of heavy metals in specific cocoa and chocolate products, with Cd limits ranging from 0.1 to 0.8 mg kg^{−1}.

Several studies demonstrated that soils, leaves, and beans from cocoa crops could contain high levels of heavy metals [6–8], which hindered product export. Soil pH, exchangeable acidity, clay percentage, organic matter, and the contents of Mn, Mg, and Fe oxides were the variables most strongly correlated with heavy metal concentrations in cocoa-producing soils [9,10]. In Colombia, Cd concentrations in soils were highly variable, ranging from 0.01 to 27 mg kg^{−1} [11].

During cocoa production, for every ton of dry beans, approximately ten tons of fresh pod shells were generated [12]. This by-product posed a problem for farmers, as the mucilage (sugary pulp) adhering to the shells attracted insects and microorganisms [13,14]. According to Lozano [15], 37,711 tons of cocoa pod shells were produced annually, highlighting the magnitude of this waste.

One of the proposed methods for restoring agricultural soils was the use of organic amendments derived from the decomposition and mineralization of plant, animal, and industrial residues [16]. These amendments improved the physical, chemical, and biological properties of soils, thereby enhancing plant production [17]. They also regulated soil pH, which limited heavy metal absorption [18,19]. In fact, most amendments improved soil pH and yield by increasing cation exchange capacity, organic matter content, and base saturation, while reducing bulk density [20].

Coffee waste, particularly spent coffee grounds (SCGs), has been proposed as a soil organic amendment. Depending on its form (composted or fresh) and application dose, SCGs could either improve or inhibit plant growth [21] due to its phytotoxic nature [17]. More recently, SCGs were shown to be a direct source of humic substances with high antioxidant capacity, capable of improving soil fertility [22]. Biochar and lime have also been tested as amendments in cocoa-producing soils, acting complementarily to reduce Cd bioaccumulation [16]. Biochar, in particular, has been widely studied for its ability to reduce heavy metal bioavailability and leaching, as its alkaline nature tends to increase soil pH [17,23,24].

Taking these considerations into account, the objective of this study was to evaluate the effect of different types of biochar derived from spent coffee grounds and cocoa pod shells on soil Cd accumulation and on the improvement of selected soil properties, with emphasis on organic carbon content, in cocoa-producing soils under *in vitro* microcosms in a climatic chamber. This study had a threefold rationale: first, cocoa represented a potential economic alternative to coca cultivation in these regions, being a crop associated with major social challenges, but the presence of bioavailable Cd in soils jeopardized this opportunity. Second, soils in sloping areas were at high risk of degradation, and the incorporation of organic carbon had the potential to provide a viable strategy to ensure the long-term sustainability of cocoa production. Third, this waste material, which was otherwise poorly

managed, was valorized, thereby reducing the risk of pests and diseases associated with its disposal.

2. Materials and Methods

Soil samples were collected from the arable layer (0–20 cm) of agricultural soils in the regions of El Zulia and Tibú, Norte de Santander (Colombia), which are characteristic of warm humid and super-humid climates [25]. The Zulia samples corresponded to cacao plantations in mountainous areas with steep slopes (>20%), whereas the Tibú samples corresponded to cacao plantations located on the river terraces (0% slope) of the Tibú River.

According to the coordinates of the studied farms, the soils corresponded to the IGAC cartographic units UCS_152 for Zulia and UCS_988 for Tibú, which described the soils as follows: Zulia soil (Figure 1) comprised deep, well-drained soils with clay loam to sandy loam textures. They exhibited low to high natural fertility, occurred under moderately humid climatic conditions, and were classified as Typic Dystrudepts (NS 161) [26]. Tibú soil (Figure 1) comprised soils ranging from shallow to deep, with drainage varying from good to poor. Textures included clay loam, sandy loam, and silty loam. They presented medium fertility, occurred under warm and humid climatic conditions, and were classified as Typic Udifluvents [26].

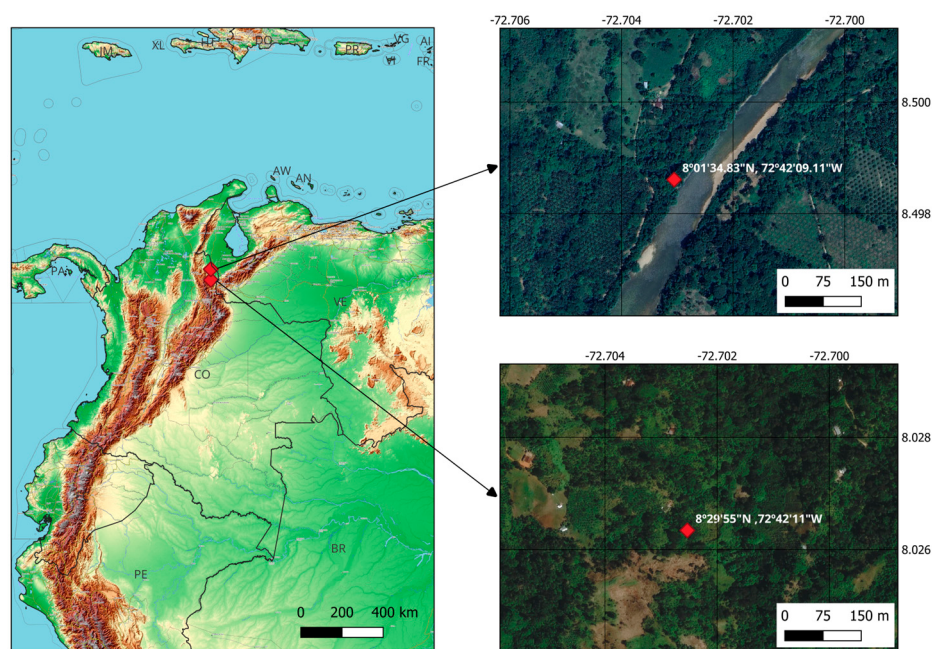


Figure 1. A map depicting the location of Tibú soil (upper) and Zulia soil (down) in Norte de Santander (Colombia).

The soil samples were air-dried and sieved (<2 mm) before use. Each analyzed soil sample was a composite mixture of three subsamples randomly collected from three randomly selected plots in each of the two cacao-growing areas. In total, each soil sample corresponded to nine subsamples measuring approximately 1 kg each.

SCG and SCGchar (biochar derived from SCG at 400 °C) were obtained following the method described by Cervera-Mata et al. [17,21]. The third amendment, Cocoachar, was produced from cocoa pod shells, which were first air-dried, then oven-dried at 50 °C, and finally pyrolyzed in a muffle furnace (Navertherm GmbH, Lilienthal, Germany) at 400 °C for 30 min. The cacao trees belonged to the species *Theobroma cacao* L. The chemical and physicochemical properties of the three amendments are presented in Table 1.

Table 1. Chemical and physicochemical properties of the organic amendments evaluated.

	SCG [27]	SCGchar [27]	Cocoachar
pH	5.4	8.4	9.53 [28]
EC (ds m ⁻¹)	9	1.78	18.06 [28]
CaCO ₃ (%)	0.15	0.34	10.1 [28]
C (%)	48	69.8	62.33 [29]
N (%)	2.29	4.253	2.36 [29]
H (%)	7.58	5.78	3.78 [29]
O (%)	4.21	20.2	3.21 [29]
C/N	21	16	27 [29]
Ash (%)	1.45	3.72	21.9 [28]

SCGs: spent coffee grounds; SCGchar: biochar derived from spent coffee grounds; Cocoachar: biochar derived from cocoa husk; EC: electrical conductivity measured at 25 °C.

The assay was carried out using dry, sieved soils (Zulia and Tibú), with five replicates at two incubation times (45 and 90 days). The mixtures were also analyzed at time 0 (baseline). Control samples corresponded to soils without amendments. The tested amendment concentrations (SCG, SCGchar, and Cocoachar) were 5, 10, and 15% ($w w^{-1}$). Considering an application area of 0.40 m² per tree and a depth of 30 cm (arable layer), these doses corresponded to 8, 16, and 24 kg of organic amendment per tree, respectively. Each sample was identified according to soil type, amendment, dose, and incubation time, and placed in 50 mL PVC bottles with perforated lids to allow for moistening every three days with distilled water. Soil moisture was maintained between the field capacity and permanent wilting point by weighing. The average addition was approximately 15 mL per sample over the entire incubation period, corresponding to 0.17 mL per day. Samples were incubated in a climatic chamber (Equitec, Madrid, Spain) at 80% relative humidity, at 30 °C during the day, and at 22 °C at night. A total of 240 samples were obtained, including controls for each incubation period. For pH, conductivity, and Cd analyses, five replicates were taken from each group (soil with/without amendment), and from those, three were randomly selected for organic carbon determination.

Soil analyses followed the methods of the American Society of Agronomy and Soil Science [30]. Granulometry was determined using the Robinson pipette method [31], and soil texture was classified using the textural triangle according to particle size distribution. Soil pH was measured in 1:2.5 ($w w^{-1}$) soil–water suspensions and in 1:5 ($w w^{-1}$) SCG–water suspensions. Electrical conductivity (EC) at 25 °C was measured in 1:5 ($w w^{-1}$) soil–water extracts. Organic carbon (OC) was determined by hot wet oxidation (the Tyurin method), and total nitrogen was analyzed using a Truspec CN Analyzer (Leco Corporation, Saint Joseph, MI, USA). Available phosphorus was measured using the Olsen–Watanabe method with a Helios Alpha spectrophotometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). Available potassium was extracted with 1 N ammonium acetate (pH = 7) and determined using a PFP7 flame photometer (Jenway, Stafford, England, UK). Available micronutrients were extracted with DTPA and determined following the method of Lindsay and Norvell [32] using Perkin-Elmer Optima 8300 ICP-OES. Cd was quantified using atomic absorption spectrophotometry (Perkin-Elmer Inc., Waltham, MA, USA), while the remaining elements were analyzed by ICP-OES. Standard calibration curves were prepared using a cadmium reference material (Merck, NIST SRM Traceable Standard Solution Cd(NO₃)₂ in 0.5 mol L⁻¹ HNO₃; 1000 mg Cd kg⁻¹, reference 1.19777.0500). All reagents were of analytical grade and supplied by Panreac Química S.L.U. (Barcelona, Spain).

Mineralogical analyses of fine earth (<2 mm) and the clay fraction (<2 µm) were performed by X-ray diffraction (XRD) using the crystalline powder method. Mineral content was estimated based on reflection factors reported by Delgado et al. [33], with a Rigaku Miniflex compact X-ray diffractometer.

Analysis of variance (ANOVA) was performed for parametric variables. The homogeneity of variance was tested using Levene's test, and normality was assessed with the Shapiro–Wilk test. When the null hypothesis was rejected, Tukey's multiple comparison test was applied. Correlation analyses were also performed. All statistical analyses were carried out using IBM SPSS Statistics v.22.0.0.0.

3. Results and Discussion

3.1. Characteristics of Cocoa Soils and Organic Amendments Assayed

Table 2 summarizes the main analytical characteristics of the cocoa soils studied, Zulia soil and Tibú soil, hereafter referred to simply as Zulia and Tibú.

Table 2. Chemical and physicochemical properties of Zulia and Tibú soils.

	Zulia	Tibú
Sand (%)	32.26	54.41
Lime (%)	38.01	24.47
Clay (%)	29.73	21.12
W-33KPa (%)	29.9	15.11
W-1500KPa (%)	15.72	6.64
Aw (mm cm ⁻¹)	1.84	1.2
pH (H ₂ O)	5.8	4.9
pH (KCl)	5.1	3.9
EC (dS m ⁻¹)	0.11	0.07
OC (%)	1.62	0.55
Total N (%)	0.15	0.23
C/N	11	4
Available Cd (mg kg ⁻¹)	0.057	0.118
Available K (cmol ⁺ kg ⁻¹)	0.3	1.3
Available P (μg g ⁻¹)	27.44	18.99

W-33KPa and W-1500KPa: water retention at −33 and −1500 kPa, respectively; Aw: available water content; OC: organic C.

The soil pH ranged from strongly acidic in Tibú (pH = 4.92, with potential toxicity due to aluminum and manganese effects [30]) to slightly acidic in Zulia (pH = 5.83). Overall, the studied soils exhibited lower pH values than those reported as adequate for cocoa cultivation by Wood and Lass [34] and Enríquez [35] (6.0–7.5 in the surface layer).

The acidity of the studied soils was influenced by farm location, as the highest rainfall in Norte de Santander was recorded in the Catatumbo region (where Zulia and Tibú are located), reaching volumes close to 5000 mm per year in areas of the municipality of Tibú [36].

Soil organic C content was higher in Zulia (1.62%) than in Tibú (0.9%). Soils could also be classified by fertility based on total nitrogen and the C/N ratio [35]. According to these parameters (Table 2), Tibú soils exhibited low fertility, making amendments necessary to improve the C/N ratio (C/N = 4.08). By contrast, Zulia soils presented higher N availability and a greater C/N ratio (C/N = 11.13).

The potassium values were 3 mmol kg⁻¹ in Zulia soils and 13 mmol kg⁻¹ in Tibú. According to Aikpokpodion [4], these values exceeded the critical level of exchangeable potassium (0.3 mmol kg⁻¹) required for cocoa plantations. Potassium is the main macronutrient demanded by cocoa, as it is a highly mobile ion that is easily lost through runoff and leaching [4]. Both soils contained significant amounts of illite in fine earth and in the clay fraction (Tables A2–A4), a potassium-rich mica. Potassium in illite occurs in the inter-layer and is relatively available to plants. Some authors consider illite to be an immediate potassium reserve readily available in the soil solution [37].

Available p values averaged $27.44 \mu\text{g g}^{-1}$ in Zulia and $18.99 \mu\text{g g}^{-1}$ in Tibú, both above the critical threshold of $10 \mu\text{g g}^{-1}$ proposed by Aikpokpodion [4] and within the high range ($>16 \mu\text{g g}^{-1}$) reported by Enríquez [35] for cocoa soils. Lower available p values ($<10 \mu\text{g g}^{-1}$), as noted by Ogunlade and Aikpokpodion [38], are typical of soils requiring fertilization, since cocoa beans remove 6–8% of soil P. León-Moreno et al. [39] also reported assimilable P values of $11.3 \mu\text{g g}^{-1}$ in soils from Norte de Santander.

The aluminum (Al) content in Zulia soils was $<12 \text{ mg kg}^{-1}$, while that in Tibú soils exceeded 50 mg kg^{-1} (Table A1). These high Al levels coincided with the low pH values observed. Calcium content showed a direct relationship with pH, as in Zulia soils, where higher Ca was associated with higher pH [37].

Extractable magnesium concentrations ranged from 80.9 ± 26.4 to $2.10 \pm 1.2 \text{ mmol kg}^{-1}$ (Table A1). Tibú soils showed Mg values below the critical levels proposed for cocoa soils: 8 mmol kg^{-1} (Aikpokpodion [4]; Enríquez [35]) and 10 mmol kg^{-1} (García-Lozano et al. [40] for Colombian soils). In contrast, Mg levels in Zulia soils exceeded these thresholds. It should be noted that Mg values extracted with DTPA differed from those reported by the cited authors, since they did not represent the truly available forms (due to methodological differences). Nonetheless, they were indicative of a trend. In soils with a $\text{pH} < 5.5$ (as in Tibú), cocoa development could be restricted due to the presence of Al, Fe, and Mn, which may cause toxicity and limit P uptake, while simultaneously reducing Ca, Mg, and Mo availability, thereby constraining cocoa production [41].

Granulometric analysis (Table 2) classified Zulia soils as medium-textured (50% sand, 10–20% silt, 30–40% clay) according to the parameters of Arvelo et al. [9]. Tibú soils contained less clay and more sand, yielding a moderately coarse texture. Mineralogical analysis (Tables A2–A4) showed the predominant mineral phases and their semi-quantification. The gravel fraction contained moderate amounts of phyllosilicates (chlorite and micas), which enhanced fertility by retaining essential cations (Mg^{2+} , K^+ , Ca^{2+}). Kaolinite was also present, particularly in the clay fraction, favoring nutrient absorption through cation exchange [42].

A notable finding was tremolite (an amphibole), which appeared as prismatic or fibrous crystals and increased with Fe content. Although asbestiform tremolite particles $>5 \mu\text{m}$ can be carcinogenic, microscopic analysis confirmed that tremolite in Zulia and Tibú soils was not fibrous (Figure A1), posing no inhalation risk [43]. Overall, texture analysis classified Zulia soils as clay loam and Tibú soils as sandy clay loam—both considered suitable for cocoa cultivation due to their aeration, drainage, and fertility, as supported by previous studies [9,34].

Regarding the amendments, they exhibited diverse physical and physicochemical characteristics (Table 1), which subsequently influenced the incubation assay. The pyrolysis of SCG produced SCGchar with higher pH (due to an increase in ash content from 1.35 to 3.72%), lower electrical conductivity, and enrichment in both C and N. These trends had already been reported for SCG biochars [44,45] and were associated with the formation of stable aromatic hydrocarbons during pyrolysis [46]. According to the literature data [28,29], Cocoachar exhibited higher electrical conductivity (18.06 dS m^{-1}) than SCG and SCGchar, together with a high carbonate and ash content and consequently a basic pH. These properties made Cocoachar suitable for use as a liming agent [28], likely influencing Cd bioavailability in soils [37].

3.2. Cadmium Remediation Assay

3.2.1. Influence of Waste Type on pH, Electrical Conductivity and Organic Carbon

The addition of SCG, SCGchar, and Cocoachar significantly increased soil pH in both Zulia and Tibú (Table 3). Among the residues tested, Cocoachar produced the greatest

effect, with maximum values observed at the 15% application rate. This response was attributable to its higher alkalinity (pH 9.54; Table 1) compared with the other two residues. The stronger liming potential of Cocoachar was likely associated with its high carbonate and bicarbonate content [28]. Soil type also significantly affected pH, as values in all treatments were lower in Tibú than in Zulia.

Table 3. pH evolution during 90 days of incubation.

		Zulia			Tibú		
		Incubation Days			Incubation Days		
		0	45	90	0	45	90
Control		6.26 ± 0.02	6.22 ± 0.13	6.12 ± 0.07	5.04 ± 0.03	5.33 ± 0.04	3.67 ± 0.01
SCG	5	6.02 ± 0.06	6.35 ± 0.09	6.23 ± 0.02	4.74 ± 0.06	5.33 ± 0.01	4.85 ± 0.36
	10	5.96 ± 0.02	6.38 ± 0.02	6.33 ± 0.04	4.77 ± 0.11	5.28 ± 0.03	5.01 ± 0.06
	15	6.15 ± 0.03	6.68 ± 0.19	6.45 ± 0.06	4.97 ± 0.02	5.37 ± 0.03	4.99 ± 0.03
SCGchar	5	6.37 ± 0.07	6.40 ± 0.12	6.23 ± 0.03	5.31 ± 0.02	5.51 ± 0.02	4.50 ± 0.04
	10	6.40 ± 0.09	6.11 ± 0.34	6.27 ± 0.36	5.41 ± 0.01	5.64 ± 0.14	4.59 ± 0.02
	15	6.76 ± 0.03	6.69 ± 0.16	6.54 ± 0.03	5.50 ± 0.02	5.88 ± 0.04	4.69 ± 0.02
Cocoachar	5	6.69 ± 0.04	6.55 ± 0.12	6.63 ± 0.01	5.72 ± 0.01	5.87 ± 0.05	4.90 ± 0.04
	10	6.82 ± 0.03	6.80 ± 0.18	6.85 ± 0.05	6.16 ± 0.06	6.23 ± 0.01	5.50 ± 0.03
	15	6.93 ± 0.01	7.15 ± 0.14	7.01 ± 0.02	6.54 ± 0.05	6.71 ± 0.01	6.14 ± 0.30
		F ratio	<i>p</i> value				
Residue		1119	<0.001				
Dose		286	<0.001				
Time		464	<0.001				
Soil		7690	<0.001				

SCGs: spent coffee grounds; SCGchar: biochar derived from spent coffee grounds; Cocoachar: biochar derived from cocoa husk.

Dose and incubation time also had significant effects, although to a lesser extent than soil type and amendment. Higher doses generally led to higher pH values, whereas incubation time showed no consistent trend. Notably, the pH of the Tibú control soil decreased sharply from 5.04 to 3.67, which could be attributed to organic matter transformations that altered soil minerals, releasing Al and causing further acidification [37]. According to Cervera-Mata et al. [27] and Pouangma Ngalani et al. [28], the addition of biochar from SCG or cocoa husk neutralized soil pH. Increasing pH levels may strongly influence Cd dynamics, an aspect that will be addressed in the following section.

Regarding electrical conductivity (EC), it followed a trend similar to that of pH, as the addition of all three amendments significantly increased EC in both soils (Table 4). Cocoachar produced the greatest increase, consistent with its high intrinsic conductivity (18 dS m^{−1}). Its application raised EC to 404 µS cm^{−1} in Zulia and 406 µS cm^{−1} in Tibú. However, this increase was of limited agronomic relevance given the region's heavy rainfall (≈5000 mm annually), which likely leaches most soluble salts from the soils.

Figure 2a,b show the influence of the different residues on organic carbon (OC) content in Zulia and Tibú soils. Soil type significantly affected OC content, with higher values in Zulia than in Tibú. The addition of all residues significantly increased OC, and the increase was proportional to the dose applied. The greatest increase was observed with 15% SCGchar. In Tibú, residue addition produced a stronger relative increase in OC, as the control sample initially had lower OC than that from Zulia. This effect was likely related to the higher intrinsic OC content of SCGchar and Cocoachar compared with the studied soils. Similar results have been reported by other authors [47–49]. A significant association was also observed between Cd and organic matter content, which will be discussed in detail in the following sections.

Table 4. Electrical conductivity ($\mu\text{S cm}^{-1}$) evolution during 90 days of incubation.

		Zulia			Tibú		
		Incubation Days			Incubation Days		
		0	45	90	0	45	90
Control		112 $\pm$ 2	262 $\pm$ 8	322 $\pm$ 117	70 $\pm$ 5	97 $\pm$ 5	158 $\pm$ 8
SCG	5	159 $\pm$ 5	176 $\pm$ 6	276 $\pm$ 6	104 $\pm$ 7	73 $\pm$ 8	76 $\pm$ 7
	10	183 $\pm$ 9	91 $\pm$ 3	204 $\pm$ 20	127 $\pm$ 7	79 $\pm$ 5	67 $\pm$ 4
	15	206 $\pm$ 3	89 $\pm$ 2	149 $\pm$ 22	154 $\pm$ 12	73 $\pm$ 2	68 $\pm$ 5
SCGchar	5	141 $\pm$ 10	236 $\pm$ 7	301 $\pm$ 10	79 $\pm$ 3	99 $\pm$ 9	147 $\pm$ 6
	10	154 $\pm$ 10	236 $\pm$ 8	282 $\pm$ 9	98 $\pm$ 4	111 $\pm$ 14	148 $\pm$ 5
	15	136 $\pm$ 6	234 $\pm$ 15	273 $\pm$ 12	87 $\pm$ 2	98 $\pm$ 3	145 $\pm$ 5
Cocoachar	5	220 $\pm$ 9	265 $\pm$ 9	303 $\pm$ 13	152 $\pm$ 2	182 $\pm$ 42	204 $\pm$ 6
	10	313 $\pm$ 19	279 $\pm$ 6	332 $\pm$ 19	263 $\pm$ 3	246 $\pm$ 7	245 $\pm$ 9
	15	404 $\pm$ 19	314 $\pm$ 10	355 $\pm$ 14	406 $\pm$ 11	279 $\pm$ 4	300 $\pm$ 10
		F ratio	<i>p</i> value				
Residue		3421	<0.001				
Dose		145	<0.001				
Time		459	<0.001				
Soil		3227	<0.001				

SCGs: spent coffee grounds; SCGchar: biochar derived from spent coffee grounds; Cocoachar: biochar derived from cocoa husk.

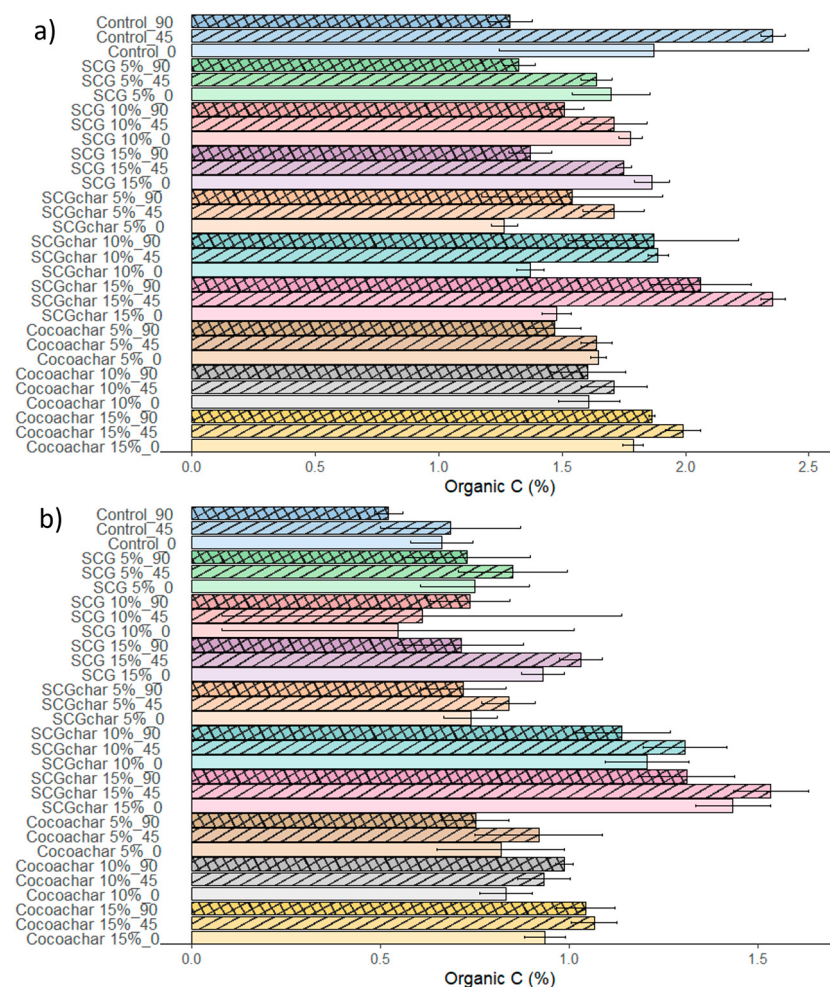


Figure 2. Organic C content in Zulia soil (a) and Tibú soil (b). SCGs: spent coffee grounds; SCGchar: biochar derived from spent coffee grounds; Cocoachar: biochar derived from cocoa husk.

3.2.2. Influence of Studied Variables on Cd Levels

The concentrations of available cadmium (Cd) in the studied soils at 0 days of incubation, without the addition of organic amendments, ranged from 0.0872 mg kg⁻¹ in Zulia to 0.1684 mg kg⁻¹ in Tibú (Figure 3). On average, these values were lower than those reported by Huauya and Huamaní [50] for cocoa soils in Norte de Santander, which had a mean Cd content of 0.53 mg kg⁻¹. Our results corresponded to the lower limit of the range reported by Bravo et al. [11] for Colombian cocoa soils (0.01–27 mg kg⁻¹).

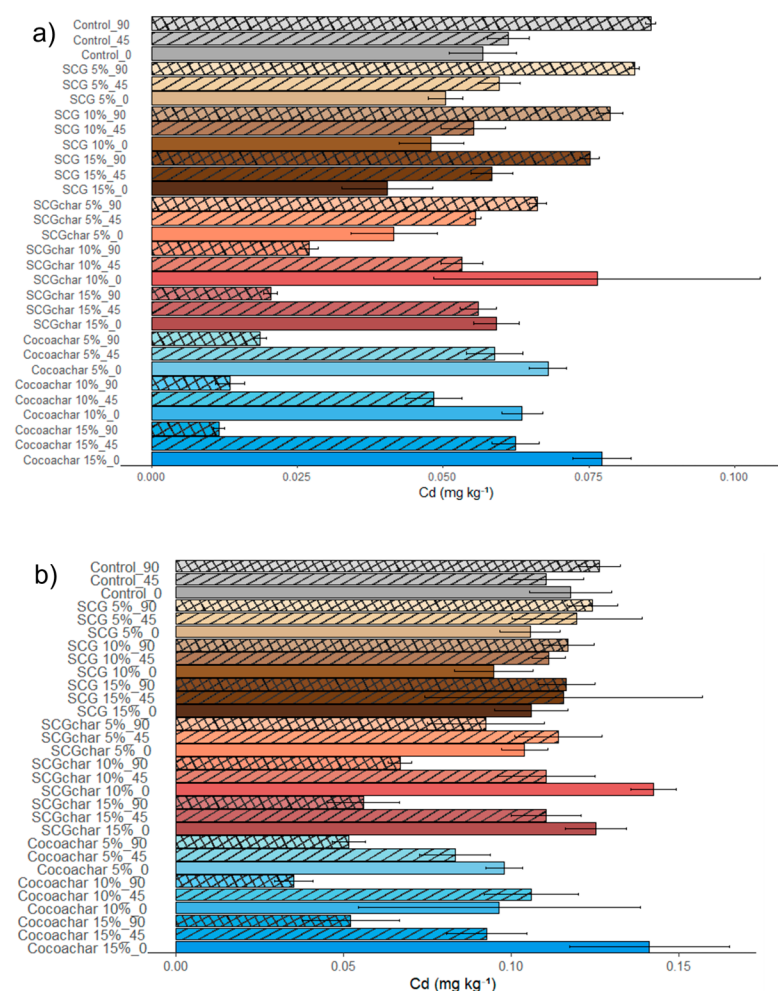


Figure 3. Available Cd content in Zulia soil (a) and Tibú soil (b).

Differences in Cd concentrations were attributed not only to pH variations but also to Mn levels—higher in Zulia soils—and to organic matter, which is known to reduce Cd toxicity. These aspects will be explored in detail in the following sections. Textural differences may also have influenced Cd content: sandy loam soils with low clay and high sand fractions tend to favor heavy metal infiltration [51]. This was the case in Tibú, which had an acidic pH and sandy loam texture. In contrast, Zulia, with its clay loam texture, presented lower Cd concentrations. Additionally, the soils of Zulia and Tibú exhibited distinct mineralogical phases with specific surface properties and charge imbalances, which could also have affected their affinity for Cd.

The addition of SCG, SCGchar, and Cocoachar significantly reduced available Cd concentrations in both soils (Figure 3a,b). In Zulia, the application of 15% SCG reduced the Cd concentration from 0.09 to 0.075 mg kg⁻¹ after 90 days of incubation. With 1% Cocoachar, the concentration of Cd decreased from 0.06 to 0.01 mg kg⁻¹, while with SCGchar it decreased to 0.02 mg kg⁻¹. In Tibú, Cd concentrations declined from

0.11 mg kg⁻¹ in the control sample to 0.05 mg kg⁻¹ with both Cocoachar and SCGchar. In general, higher application doses resulted in lower Cd availability, and a significant reduction in soil Cd was also observed over the incubation period.

Regarding the remediation effect of SCG, our group previously reported that the addition of high doses of SCG (7.5–15%) decreased mean Cd concentrations in lettuce cultivated with this bio-residue [52]. Similarly, other studies [53] demonstrated that the addition of both SCG and SCGchar reduced Cd bioavailability in soils. Concerning cocoa husk biochar, our findings were consistent with those of Pinzón-Núñez et al. [24], who evaluated its use to reduce soil Cd. These authors observed that the application of cocoa husk biochar lowered the available Cd from 1.74 to 1.40 mg kg⁻¹.

One of the mechanisms by which biochar reduced bioavailable Cd was through its capacity to adsorb ions and molecules [54]. Functional groups on the surface of biochar likely controlled heavy metals by forming specific complexes in soil [53]. Specifically, Cd adsorption followed the Langmuir adsorption model. According to Pinzón-Núñez et al. [24], the maximum sorption capacities of Cd were 21.58 mg g⁻¹ and 19.21 mg g⁻¹ for cocoa husk biochars produced at 700 °C and 600 °C, respectively. These results suggested that cocoa husk biochar represented a promising alternative for Cd remediation. This effect may be attributed to the high specific surface area of biochar, which can range from 1–2 m² g⁻¹ to 1331 m² g⁻¹ depending on feedstock and pyrolysis conditions. In addition, biochar contributed to bioremediation by altering the chemical speciation of metals [55].

To limit Cd mobility, the application of biochar can be effective by increasing soil pH [56,57]. Saleem et al. [57] reported that Cd immobilization in soil increased and its bioavailability decreased when biochar was applied at rates of 1–2%. It should be noted that the most significant predictor of Cd adsorption is soil acidity [24]. An alkaline pH promotes the reduction in leachable and exchangeable Cd fractions [58]. In particular, Cd adsorption is greater when the pH of cocoa husk-derived biochar ranges between 7 and 9 [24]. Accordingly, in the soils of Zulía and Tibú, an increase in pH following the addition of organic amendments (Table 2) was associated with a decrease in Cd concentrations (Figure 3), likely due to changes in Cd mobility driven by increased basicity and organic matter content. In the case of the Tibú soil, which contained high Al concentrations (52.45 mg kg⁻¹), one possible explanation is that Cd immobilization occurred through Al–OH–Cd ternary complexation [59]. A similar relationship was previously reported by Al-Wabel et al. [60] in mine-contaminated agricultural soils used for maize production in Saudi Arabia. Pauget et al. [61] also found that increasing soil pH (from 5 to 7) reduced Cd levels from 76% to 93%. Moreover, they observed that higher organic matter content decreased Cd availability, while clay content had no effect.

4. Conclusions

The soils of cocoa-producing farms in the Zulía and Tibú region, based on their textural characteristics, are suitable for cocoa cultivation. However, they generally exhibit an acidic pH that promotes the uptake of heavy metals, particularly cadmium, with concentrations in the sampled soils exceeding the levels considered phytotoxic. Such Cd levels can be explained by factors including pH, organic carbon (OC), and the concentrations of Al, Fe, and Mn.

With respect to soil remediation strategies, the increase in pH resulting from the addition of biochar (SCGchar and Cocoachar) reduced Cd concentrations, with Cocoachar demonstrating a strong capacity to decrease the bioavailability of Cd in contaminated soils. Moreover, the addition of SCGs, SCGchar, and Cocoachar exerted markedly different effects on the physicochemical and nutritional properties of the two soils tested.

Taken together, the significance of this study lies in the use of a contaminant by-product (cocoa pod shells) that can be transformed into biochar and applied to mitigate Cd accumulation in agricultural soils. This represents a practical and low-cost solution for farmers, many of whom have limited access to other remediation products due to their high cost. In addition, the application of biochar to soils is an important strategy for replenishing organic matter in currently degraded soils.

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Abbreviations

The following abbreviations are used in this manuscript:

SCGs	Spent coffee grounds
EC	Electrical conductivity
OC	Organic carbon

Appendix A

Table A1. Extraction of minerals with DTPA in soils of Zulia and Tibú.

(mg kg ^{−1})	Zulia	Tibú
Al	5.37 ± 5.77	52.45 ± 4.97
Ca	645.2 ± 166.4	0
Cr	0.02 ± 0.03	0
Cu	1.6 ± 1.21	0.69 ± 0.21
Fe	89.55 ± 0.93	85.69 ± 21.91
K	40.35 ± 44.73	1.8 ± 1.66
Mg	415.6 ± 115.6	12.61 ± 6.6
Mn	30.22 ± 19.45	5.04 ± 1.25
Mo	0.04 ± 0.07	0.06 ± 0.07
Na	195.8 ± 38.56	76.03 ± 86.41
Ni	0.71 ± 0.37	0.08 ± 0.01
P	11.95 ± 3.02	5.07 ± 1.56
Pb	0.11 ± 0.19	0.74 ± 0.16
S	44.3 ± 41.9	26.9 ± 12.2
Zn	7.97 ± 7.11	0.01 ± 0.01

Table A2. Semiquantitative mineralogical analysis in the gravel fraction (>2 mm) of the studied soil samples.

	Zulia			Tibú		
	1	2	3	1	2	3
Chlorite	x	x	x	x	x	x
Illite (K-mica)	x	x	x	xx	x	xx
Tremolite	xxx	xxx	xxx	x	x	x
Quartz	xxx	xxx	xxx	xxxx	xxxx	xxxx
Kaolinite				x	x	x
K Feldespatite	x	x	x	xx	xx	xx
Plagioclass	xxx	xxx	xxx	xx	xx	x
Iron oxide					x	x
Minerals						
Interstratified		x	x		x	x

Content key: x, <5%; xx, 5–15%; xxx, 15–30%; xxxx, 30–50%; xxxxx, >50%. Chlorite (Mg, Fe)₃(Si, Al)₄O₁₀(OH)₂·(Mg, Fe)₃(OH)₆; Illite (K-mica) (K, H₃O)(Al, Mg, Fe)₂(Si, Al)₄O₁₀[(OH)₂, (H₂O)]; Tremolite (Ca₂Mg₅Si₈O₂₂(OH)₂); Quartz SiO₂; Kaolinite (Al₄Si₄O₁₀(OH)₈; Feldespatite of K (KAlSi₃O₈); Plagioclass (Na, Ca)(Si, Al)₃O₈; Iron oxide Fe₂O₃.

Table A3. Semiquantitative mineralogical analysis in the fine-earth fraction (<2 mm) of the studied soil samples.

Soil Type		Region				
Fine Earth	Zulia			Tibú		
	1	2	3	1	2	3
Chlorite	xx	x	xx	xx	xx	xx
Illite (K-mica)	x	x	x	x	x	x
Tremolite	xx	x	x	x	x	x
Quartz	xxx	xxxx	xx	xxxx	xxxx	xxxx
Kaolinite	x	x	x	x	x	x
K Feldespatite	x	x	x	xx	xx	xx
Plagioclass	xxx	x	xxx	xx	xx	x
Iron oxide	x	x	x	x	x	x
Minerals						
interstratified	x	x	x	x	x	x
Smectite		xx				
Talc		x				

Content key: x, <5%; xx, 5–15%; xxx, 15–30%; xxxx, 30–50%; xxxxx, >50%. Chlorite (Mg, Fe)₃(Si, Al)₄O₁₀(OH)₂·(Mg, Fe)₃(OH)₆; Illite (K-mica) (K, H₃O)(Al, Mg, Fe)₂(Si, Al)₄O₁₀[(OH)₂, (H₂O)]; Tremolite (Ca₂Mg₅Si₈O₂₂(OH)₂); Quartz SiO₂; Kaolinite (Al₄Si₄O₁₀(OH)₈; Feldespatite of K (KAlSi₃O₈); Plagioclass (Na, Ca)(Si, Al)₃O₈; Iron oxide Fe₂O₃.

Table A4. Semiquantitative mineralogical analysis of the phyllosilicates in the clay fraction (<2 µm) of the studied soil samples.

Soil type		Region				
Clay Oriented Aggregate	Zulia			Tibú		
	1	2	3	1	2	3
Chlorite	x	xx	x	xx	xx	xx
Illite (K-mica)	xxxx	x	xxxx	xx	xx	xx
Kaolinite	xxxx	xxxx	xxxx	xxxx	xxxx	xxxx
Minerals interstratified	xx	xxx	xx	xx	xx	xx
Smectita	x	x	xx	x		

Content key: x, <5%; xx, 5–15%; xxx, 15–30%; xxxx, 30–50%. xxxxx, >50%. Chlorite (Mg, Fe)₃(Si, Al)₄O₁₀(OH)₂·(Mg, Fe)₃(OH)₆; Illite (K-mica) (K, H₃O)(Al, Mg, Fe)₂(Si, Al)₄O₁₀[(OH)₂, (H₂O)]; Kaolinite (Al₄Si₄O₁₀(OH)₈; Smectite Mg₃Si₄O₁₀(OH)₂.

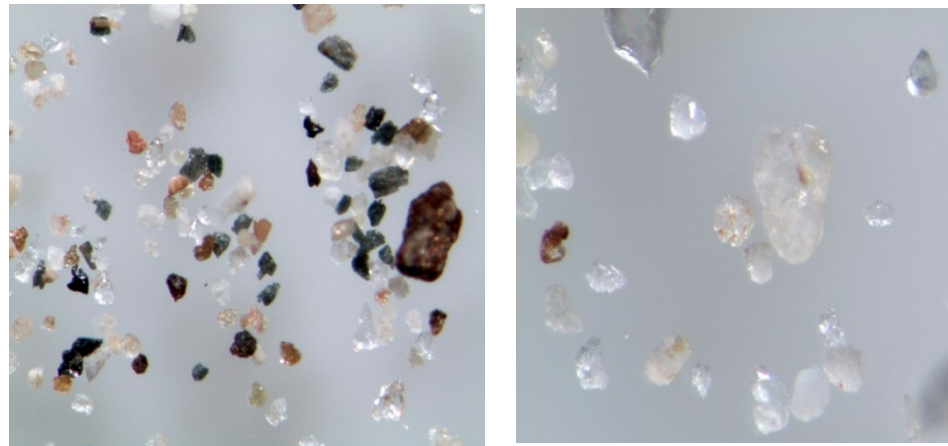


Figure A1. Photographs of fine sand (50–200 µm) soil from Zulía (left) and fine sand (50–200 µm) soil from Tibú (right).

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