soil systems

MDPI

Article

Natural and Anthropogenic Sources of Cadmium in Cacao Crop Soils of Santander, Colombia

Valentina Joya-Barrero [1], Carme Huguet [1,*] and Jillian Pearse [2]

[1] Department of Geosciences, Los Andes University, Bogotá 111711, Colombia
[2] Department of Geological Sciences, California State University, Long Beach, CA 90840, USA
* Correspondence: m.huguet@uniandes.edu.co

Abstract: Elevated cadmium (Cd) levels in cacao products have been detected in a major cacao-producing region of Colombia, with concentrations well above those permitted for export and posing a potential threat to human health. Geochemical and petrographic analyses of fertilizer, soil and rocks from three farms were used to determine the origin of Cd. Parent rocks were the main source of the Cd in soils, while organic fertilizer may have further contributed to elevated metal content in one farm. High Cd levels in the organic fertilizer were most likely due to bioaccumulation, since it was sourced from animals in the same area. Even though the soil pH range, elevated OM content and the presence of Mn and K diminish bioavailability, the extremely high Cd content in soils results nonetheless in significant uptake by the plants and subsequent accumulation in cocoa beans. Traditional methods to reduce Cd adsorption, such as the addition of calcium, will not be effective in this case. Instead, the selection of cacao species that are naturally low accumulators and amendment with soil microorganisms with mineralization and biotransformation capabilities, as well as testing of fertilizers before application, could all be cost-effective solutions to reduce Cd in the final product.

Keywords: cadmium; cacao; soil analysis; autochthonous origin of Cd; allochthonous origin of Cd

check for updates

Citation: Joya-Barrero, V.; Huguet, C.; Pearse, J. Natural and Anthropogenic Sources of Cadmium in Cacao Crop Soils of Santander, Colombia. *Soil Syst.* **2023**, *7*, 12. https://doi.org/10.3390/soilsystems7010012

Academic Editors: Antonella Lavini and Mohamed Houssemeddine Sellami

Received: 28 November 2022
Revised: 10 January 2023
Accepted: 11 January 2023
Published: 6 February 2023

1. Introduction

Cadmium (Cd) is one of the elements that occur naturally in the crust, with reported concentrations of 0.1–0.5 ppm [1]. Because of its mobility in soils, it is readily absorbed by plants despite not having a metabolic function [2,3]. As a non-essential heavy metal, it can cause toxic effects in plants, animals and humans, whether due to acute or chronic exposure and even at low concentrations, e.g., [1–3]. Cadmium is considered to be one of the most toxic metals for humans as it exhibits adverse effects on all biological processes, acting as a precursor of various cancers, oxidative stress and kidney malfunction, e.g., [1–4]. It is classified as a Group 1 carcinogen as it has been associated with lung and pancreatic cancer [5]. The metal can accumulate in organisms, particularly in bone and kidney tissue, leading to notorious health impacts through dietary consumption [5]. As the metal does not biodegrade, it also bioaccumulates through the food web, eventually posing a health hazard for humans, e.g., [2–4]. Chocolate and cacao powder with elevated Cd levels can be an important source of human exposure to the metal, impacting the health of consumers, e.g., [6].

High levels of Cd in soils of cacao farms pose one of the greatest challenges for producing safe cocoa products in South and Central American countries [7–10]. Latin America and the Caribbean show high Cd content in cacao beans with mean values higher than those found in Africa and Asia and above the acceptable health limits proposed internationally (Figure 1; [7–10]). The study area displays abnormally high Cd concentrations in beans, well above average for the Latin America and Caribbean (LAC) region and the acceptable level in beans (Figure 1). Aside from the potential health impacts, starting in January 2020 the European Union enforced a new regulation for the maximum values for Cd concentrations in cocoa-based products, which has put a strain on South and Central American cacao producers [11].

Since Colombia is one of the world's major cacao producers, contributing 1.5% of the global market, the high Cd concentration will have a sizeable impact on the country's economy, e.g., [12]. Santander is a well-known cacao region in Colombia, historically recognized for having vast areas of cacao crops (62,500 ha) of excellent quality and contributing the biggest portion of cacao for export, e.g., [13]. Recently, cacao has been highlighted in the context of post-conflict Colombia as the main substitution crop for coca plantations, with 25,000 ha having already been transformed from illegal crops into cacao [13]. It is thus essential to understand the possible factors that may increase Cd in soils so that new cacao farms are not established in unsuitable areas.

Cadmium can originate from bedrock, erosional-depositional and recycling processes, as well as from anthropogenic sources [14–16]. Cd has high mobility through sediment flows and erosion processes by water and wind, and material translocation, which results in accumulation in sedimentary environments [17,18]. Moreover, concentrations of Cd are higher in sedimentary rocks since this metal can also be easily adsorbed into fine particles and porosity sites [16,19]. The Cd content tends to be higher in fine-grained acidic sedimentary rocks [16,20,21]. The relative accumulation of Cd in sedimentary environments may also be due to the degassing of the Earth and mantle processes, in which excess volatile elements such as Cd are liberated and accumulated within empty spaces [22].

The anthropogenic sources of Cd are mainly related to the addition of both organic and inorganic fertilizers, and the potential contamination from mining or construction sites, e.g., [20]. Cd can also be reinserted into the soil through the plant's leaves or branches, as farmers leave plant debris as a fertilizer, thus recycling the metal into the ground, e.g., [6,9].

Even though other forms of Cd co-exist with Cd^{2+}, contributing to the total content of the metal in the bedrock and soil, only the ion is available for plant uptake [6,8,15]. The parent rock and the demineralization and weathering processes during pedogenesis will determine the amount of bioavailable Cd^{2+} in soils [23,24]. Soils inherit many of the bedrocks characteristics and retain a large portion of its elements; for example, carbonate rocks with high Cd content have been shown to produce soils enriched in the metal after pedogenesis [24]. Several soil properties can regulate Cd bioavailability; while high electrical conductivity and salinity, as well as loamy and clayey soil textures, result in an increase, near-neutral pH range, medium-high organic matter content or the presence of certain elements (e.g., Mn, K) reduce its availability [4,25].

The country's production is year-round and consists mainly of Criollo and Trinitario varieties, which are known for their fine chocolate flavor but relatively low yield [26]. The *Theobroma cacao* plant bioaccumulates Cd, which is easily absorbed by its roots from soil and water in its available Cd^{2+} form along with the other nutrients the plant needs, accumulating then within the structures of the plant, e.g., [6,8,15]. The accumulation occurs preferentially in cacao beans, followed by fruit shells, and the smallest quantity accumulates in leaves [6,7]. It has been found that in some cases the proportion of Cd content in soil and beans is about 1:4, but that even if the proportion varies, there is always substantial accumulation in beans compared to soil concentration [6,7].

Previous studies show that the concentration of Cd in plant structures can vary depending on the farm location and the soil characteristics, e.g., [9,21]. In a recent study of Colombian cacao soils, a mean level of Cd of 1.43 mg/kg for a total of 1837 soils was reported, well above the natural concentrations found in soils worldwide [27]. Santander shows the second highest Cd soil concentration, with a mean of 1.90 mg/kg and a maximum value of 27 mg/kg Cd—far beyond those of other regions in the country [27]. Perhaps not surprisingly, average Cd concentrations as high as 4.3 mg/kg for beans have been reported in the area, far exceeding the threshold of 0.60 mg/kg applied for cacao bean exports to the EU and the maximum level of 1.3 mg/kg for cocoa powder proposed by the Codex Committee on Contaminants in Food (CCCF) (Figure 1; [14,27]).

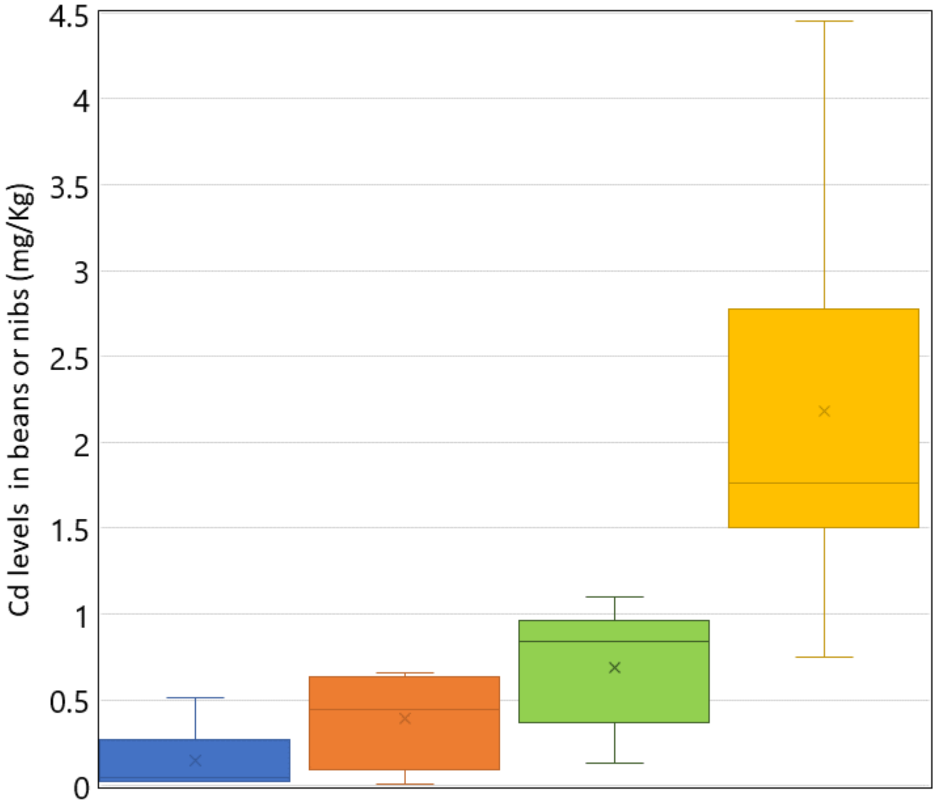

Figure 1. Cadmium levels in cacao beans and nibs from Africa, Asia, Latin America and the Caribbean (LAC) and San Vicente de Chucurí (SVC) (data from [10,14]). Overlaid: the ideal maximum level of 0.5 mg/kg (IML, dashed grey line); the acceptable limit in beans of 0.8 mg/kg (ALB, dashed black line); and the maximum proposed limit of 1.3 mg/kg Cd for cocoa powder (100% total cocoa solids on a dry matter basis) set by the Codex Committee on Contaminants in Food (MPL, dashed red line) [14,28].

Our aim was to improve the understanding of the possible natural and anthropogenic sources of the metal in the study area. We also analyzed soil parameters that may regulate the bioavailability of the metal to gain a better insight into the problem and be able to propose better solutions. Providing a sound baseline of Cd levels and sources is a first step towards better management practices and, when needed, remediation strategies in the area. Beyond improving the situation in the study area, it is crucial to establish the conditions for low Cd in soils to aid with the planned cacao farm expansion to replace illicit crops.

2. Materials and Methods

2.1. Study Area

San Vicente de Chucurí is located in the Northeastern region of the department of Santander, Colombia, and it is known as the "cocoa capital of Colombia" (Figure 2). The annual mean temperature is 23.7 °C and average annual rainfall is 1820 mm [14] with a tropical rainforest climate according to the Köppen-Geiger classification. The main soil types in the area are Humic Cambisols (CMu) in both low (0–600 m.a.s.l.) and mid-altitude (600–900 m.a.s.l.) terrains and Umbric Leptosols (LPu) in high altitudes (900–1200 m.a.s.l.) [14]. All our study sites fall in the CMu soils category, with some soil differentiation and the presence of a humus-rich horizon, considered ideal for cacao cultivation.

The three farms used in the study are over the geological unit b6b6-Sm within the "Simití" formation, which is made up mainly of laminated black claystones and carbonaceous and locally calcareous fine-grained rocks, with a significant presence of calcareous concretions (Figure 2; [29,30]).

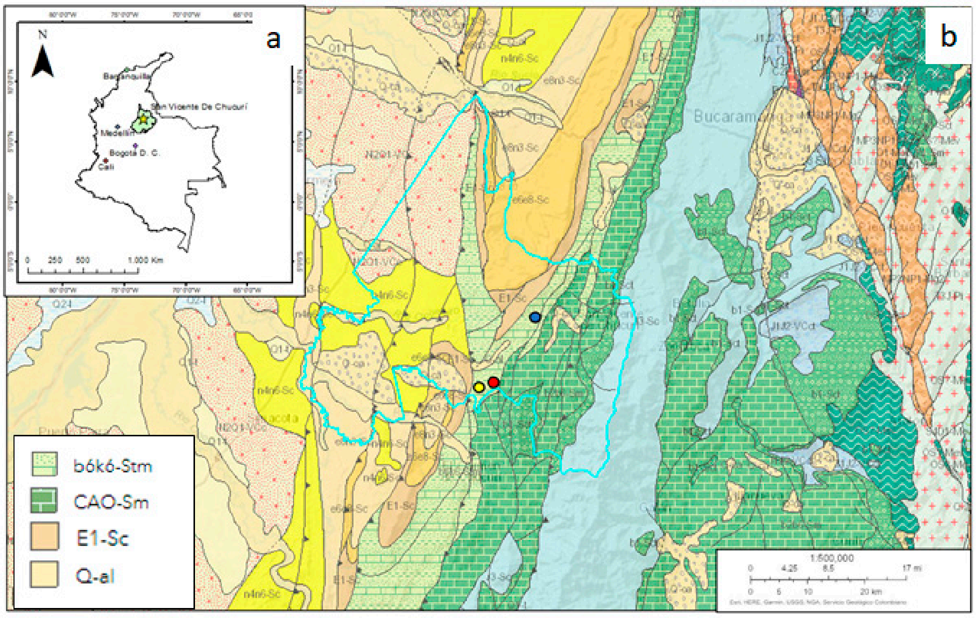

Figure 2. Maps of the study area. (**a**) Map of Colombia with the country's main cities shown. The department of Santander is highlighted in green with a star indicating the location of San Vicente de Chucurí. (**b**) Geological map of San Vicente de Chucurí [29,30] with the municipality limits indicated by the light blue line. Sample collection sites Farm 1 (red dot), Farm 2 (yellow dot) and Farm 3 (blue dot) are indicated.

2.2. Sample Collection

A total of 37 samples (23 soils, 12 source rocks and 2 fertilizers) were collected and analyzed at three different farms in the study area (Figure 2). All soil samples were taken at a depth of 30 cm and each weighed approximately 1000 g. Samples from fertilizers in Farms 1 and 2 were also collected. An organic fertilizer was used regularly (subjective dose applied 1 to 2 times a month depending on rainfall) in Farm 1 and an inorganic one in Farm 2 (the last application was a year before sampling). The organic fertilizer was composed of cocoa and banana tree leaf litter, chicken and pig manure (animals were fed with food residues and organic matter from crops grown in the farm soils) and topsoil, all collected within the farm and managed by the farmer using a rustic composting system to transform the residues. We did not measure the nutrient content of the organic fertilizer as we focused solely on its Cd content; however, as its main component was chicken manure, the nutrient content could be similar to that measured in other uses of chicken manure: 27% raw protein, 18% mineral matter, 4% Calcium (Ca) and 2% phosphorous (P).

The inorganic fertilizer was Diammonium Phosphate (DAP) which is commercially sold. This fertilizer is used as a source of phosphorus (P) and nitrogen (N) for plant nutrition. It is highly soluble and has an alkaline pH that develops around the dissolving granules. Its composition is 18% total nitrogen (N), 18% ammoniacal nitrogen (NH_4) and 46% water-soluble phosphorus (P_2O_5). This fertilizer was preferred as it was less aggressive with seedlings and was recommended by the farmers' technical assistants.

In Farms 1 and 2, which are plantations of less than 1 ha, the sampling was carried out in transects with a distance of around 8 m between each point. In the first farm we collected a rock sample at each soil sampling point, while in the second plantation only one rock sample was collected for each transect. In Farm 3, which is more extensive (~15 ha), but also more homogeneous, five soil samples were taken using randomized sampling with a distance of around 12 m between each point. No rock samples were collected in this case since soil was homogenized in the first 2 m and rock fragments were not present. As the third farm is located over the same geological unit, we expect the parental rock material to be of the same composition as both the other farms.

2.3. Petrographic Analysis

Petrographic analysis was performed on 3 rock samples (from Farms 1 and 2) and 3 soils (one from each farm), selected for having the highest Cd concentrations. The samples were processed into 6 polished thin-sections (of 30 µm thickness), and sent for analysis at Alicante University, Spain. Samples were studied using a ZEISS Assioskop microscope and pictures were taken with a Photometrics CoolSNAPcf digital camera and the RS ImageTM v.1.8.6 software (Seattle, WA, USA). Mineral chemical composition was established using a scanning electron microscope (SEM). Backscattered Electro (BSE) and X-ray spectroscopy (EDS) images were obtained using a Hitachi microscope, model S3000N at an accelerating voltage of 20 kV.

The XMET-7000 manual specifies all the Limits of Detection (LOD) in parts per million (ppm), but there is no given LOD for Cd measurements [30]. The Limit of Detection relates to repeatability, but does not indicate the instrument accuracy. LODs are dependent on matrix interferences, overlapping elements, level of statistical confidence and testing time [31]. To reduce potential effects on instrument precision, we used longer than recommended testing times (5 min) and verified that the statistical confidence level was high.

2.4. Soil Analysis

A LAQUAact-PC110 probe was used to measure the pH in soil samples. To do so, 1 g of humid soil was placed in 9 mL of distilled water and the solution was mixed for 2 min in a vortex and left to rest for 30 min. The probe was placed in the supernatant and pH was measured 3 times.

In order to quantify humidity, 100 g of each soil were placed in the oven at 45 °C for three days. The soil was re-weighed and the difference in mass was assumed to be water content, e.g., [31].

To measure the organic matter (OM) content, the same dry soil samples were then placed in the oven at a temperature of 250 °C for 24 h. Samples were then weighted and the difference in mass was assumed to be combusted OM, e.g., [31].

For carbonate content, the dry-inorganic soil samples were placed in a muffle at a temperature of 450 °C for 24 h. Samples were then weighed, and the mass value of carbonate was calculated from the mass difference, e.g., [31].

All instruments within the laboratories of the Universidad de los Andes used for the sample analysis above are calibrated on a biweekly or monthly basis by the department technicians.

2.5. X-ray Fluorescence (XRF) Measurements

Element composition was measured in the soil, fertilizer and rock samples. For soils and fertilizers, 250 g of fresh sample were dried in an oven at 45 °C for three days in order to remove moisture, as the presence of water may influence the signal intensity and increase instrumental error [32]. Dry samples were homogenized using a mortar and pestle and divided in four; then, two opposite quadrants were mixed and rearranged again as a circle. This process was repeated as many times as needed until reaching ~2 g of sample for analysis. This was performed in order to minimize measurement variation due to sample heterogeneity. The rocks were washed and measured directly.

The chemical elements from Beryl (Z = 4) to Uranium (Z = 92) were measured by XRF (X-Ray Fluorescence) using an Oxford XRF 7500 probe. All samples were measured with an XRF gun (XMET-7000) with the preprogrammed soil setting for soils and the mine setting for rock samples. Each sample was measured a minimum of three times and reported values in the present study represent the mean measurement with error bars shown. The procedure with the organic and inorganic fertilizers was the same as for the soil samples, only changing the preprogrammed setting in the XRF gun to the standard element set. Soil samples show smaller errors, most likely due to the removal of humidity and the grinding process which homogenized the samples and enabled a more uniform XRF reading, e.g., [33,34]. For the rock samples the error is generally larger, most likely caused by measuring directly on solid rock. Nevertheless, these measurements on direct rock are reliable as specified by the manufacturer and still fall within an acceptable standard error 3 [32–34].

2.6. Statistical Analysis

A Principal Component Analysis (PCA) was performed on the normalized soil parameters studied to provide a general view of the variability within the studied soils and the main factors determining Cd concentrations. The data were normalized using the corresponding mean and standard deviation as follows:

$$\text{Normalized data} = (\text{Data value} - \text{Data mean})/\text{Stdev} \tag{1}$$

This allows the comparison of data that have different units.

A paired-group (UPGMA) Euclidean distance cluster analysis was performed to understand data grouping of the individual samples. All analyses were performed with PAST 4.07 [35].

3. Results

3.1. Cadmium Concentrations

Measured Cd values ranged from 8 mg/kg ± 7 for soil in Farm 2 to 90 mg/kg ± 7 in a rock sample of Farm 1 (Figure 3). The highest value (90 mg/kg ± 7) was found in a rock fragment collected in Farm 1, which was at double the average Cd concentration of all other rock samples analyzed (50 mg/kg ± 3.8; Figure 3). While all farms display a range of Cd concentrations and thus values are not significantly different between farms, generally the highest concentrations are detected in Farm 1 (42 ± 19.3 mg/kg), intermediate ones are found in Farm 2 (32 ± 13.3 mg/kg) and lower ones in Farm 3 (25 ± 11.7 mg/kg) (Figure 3; Table S1).

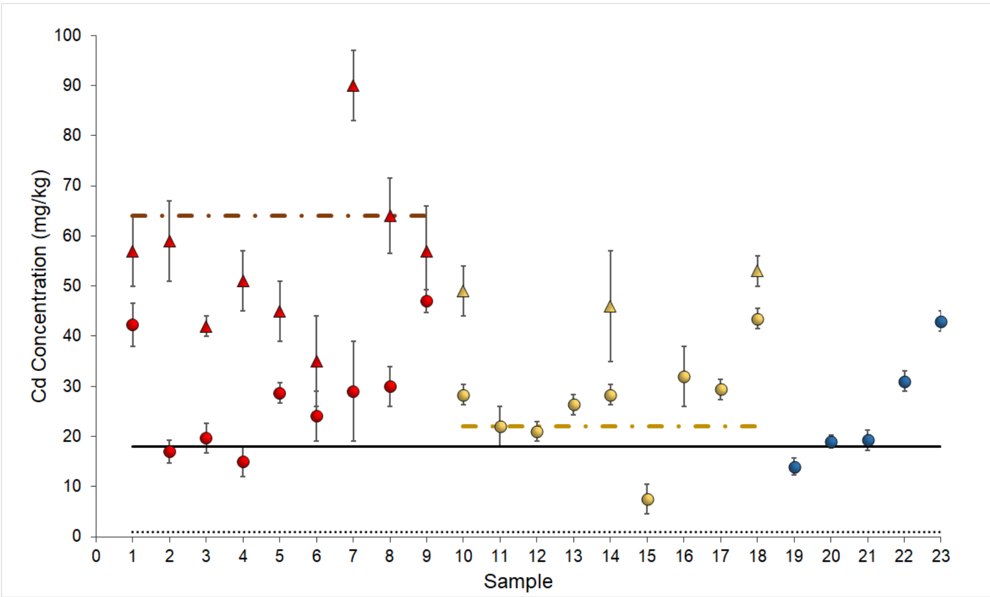

Figure 3. Cadmium concentration in soil (circles), rock samples (triangles), concentrations of organic (red dashed line) and chemical fertilizers (yellow dashed line). Red is for samples from Farm 1, yellow Farm 2 and blue Farm 3. The Cd critical threshold for human health risks (18 mg/kg; continuous line [36,37]) and the widely used threshold values for Cd concentrations in agricultural soils (1 mg/kg, dotted line; [9,27] and references therein) are indicated.

Based on the farms being in the same geological setting, if we instead separate matrices we find that the rocks have a significantly higher Cd average (54 mg/kg ± 13.9) than soils

(27 mg/kg ± 10.1) (Figure 3; Table S1). Since the sampling of rocks was uneven between farms, and rocks have the highest Cd concentrations, when averaging only soils we find no significant difference between the studied Farms (Figure 3; Table S1): Cd levels for Farm 1 were found to be 28 ± 10.8 mg/kg, Farm 2 slightly lower at 26 ± 9.6 mg/kg and in Farm 3 Cd concentrations were at 25 ± 11.7 mg/kg.

In Farm 1, an organic fertilizer was used and it had the second highest Cd concentration in the sample set (64 ± 2 mg/kg; Figure 3). In the case of Farm 2, the inorganic fertilizer applied one year prior to the study had Cd values of 22 ± 2 mg/kg (Figure 3; Table S1).

All soils displayed values above the reported "natural" Cd levels in agricultural soils of 1 mg/kg ([27] and references therein). The critical threshold for human health risks (18 mg/kg; [36,37]) was also surpassed by most soils, with the exception of soil 4 in Farm 1, soil 15 in Farm 2 and soil 19 in Farm 3 (Figure 3; Table S1).

3.2. Petrographic Analysis

Based on the petrographic analysis the bedrock types in the area were classified as limestone, marl and shale, and in all cases, rocks were found to be carbonate-rich (Figure 4a). This is mostly related to them being fossil-rich; abundant fragments of sea urchins and minor bivalves, in both cases built from calcium carbonate, can be observed in thin sections (Figure 4b).

The Backscattered electron images (BSE) of rock sample thin sections indicate an abundance of calcite (Cc), minor quartz (Qz) and some hematite (Fe_2O_3) and barite ($BaSO_4$) (Figure 4c). The rocks analyzed also have fine-grained quartz and accessory minerals are zircons and frankolite (carbonate-fluorapatite) (not shown).

The soil thin sections revealed an abundance of organic matter (OM) as well as unconsolidated carbonates (Figure 4d). We observe microaggregates of OM to also contain fragments of carbonate (Figure 4d).

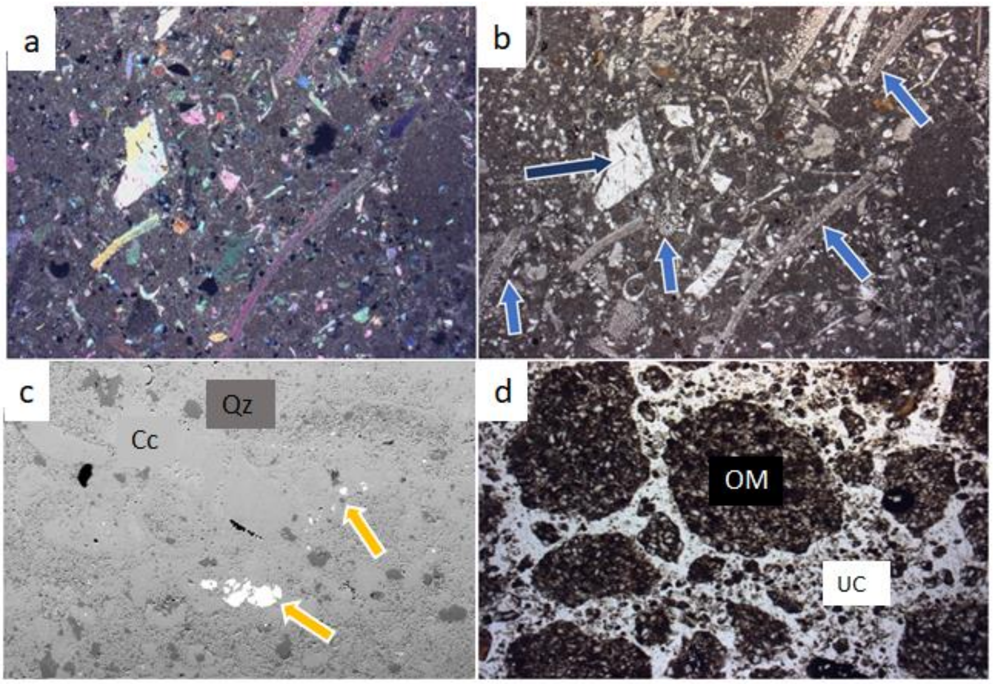

Figure 4. Petrographic analysis images of (**a**) cross polarized light (XPL) image of rock sample thin-section; (**b**) plane polarized light (PPL) of rock sample thin-section with abundant fragments of sea urchins (light blue arrows) and minor bivalves (dark blue arrow); (**c**) Backscattered electron image (BSE) of rock sample thin-section indicate abundance in calcite (Cc), minor quartz (Qz) and some hematite (Fe_2O_3) and barite ($BaSO_4$) grains (yellow arrows); (**d**) soil sample thin-section showing mostly unconsolidated carbonate (UC) with organic matter (OM).

4. Discussion

Santander is a well-known region for the cultivation of cacao and has been historically recognized for having cacao crops of great extension and quality, representing 40 to 45% of Colombian production. Addressing elevated Cd content is crucial not only as a public health concern, but also for the potentially negative impact it will have on cacao exports, a key economic sector for the region [26,28]. Moreover, since there are plans to expand cacao farming in the country as a substitute for illicit crops, it is paramount to establish the conditions that determine the presence and bioavailability of Cd in soils. Understanding the origin and fluxes of Cd can give insight into the best management strategies for the soil and translate into practical solutions for farmers in the region. Cadmium can be of autochthonous and/or allochthonous origin and sources include bedrock, erosional-depositional and recycling processes, as well as anthropogenic input; moreover, several soil properties regulate its bioavailability [4,6,15,25].

4.1. Cadmium Levels in the Study Area

All the samples analyzed show elevated Cd values compared to both international standards and national averages (Figures 1 and 3; [27]). In fact, the entire west flank of the Colombian Eastern cordillera shows significantly higher Cd values in sediments and soils (ranging from 1.8 to 74 mg/kg) than any other region in the country, resulting in a potential health hazard (Figure 5). Even though the study farms are within an area with no reported geochemical Cd values, we can extrapolate high concentrations from neighboring regions, which have concentrations falling in the ranges of 1.8 to 4.6 mg/kg and 4.6 to 74 mg/kg (in sediments; Figure 5). Additionally, values reported in other farms of San Vicente show average Cd concentrations of 3.3 mg/kg, with farms on the east side of the municipality having values around 2.1 to 4.3 mg/kg of total Cd and those on the west side having a maximum of around 2.5 mg/kg total and 0.1 mg/kg of available Cd [14].

The parent rock in the study area presents unusually high Cd concentrations with values of up to 3 times what was previously reported in Central Colombia [38]. Previously reported anomalously high Cd levels in rocks range between 8.15 mg/kg and 21.4 mg/kg worldwide ([21] and references therein), which is consistent with our findings of extremely elevated Cd concentrations in the study area rocks. Rock Cd values in the studied farms, even though always unusually elevated, vary from 30 to 50 mg/kg, suggesting heterogeneity of the parent material's metal content (Figure 3). Thus, the adsorption of Cd into fine particles and porosity sites varied within the Simití formation, probably because of the different types of sedimentary rocks and micro-meso lithification environments (Figure 1; [16,19]).

Total Cd content in cacao soils has been found to be mainly present as residual and oxidable fractions, associated with the weathering of the bedrock and other pedogenesis processes, so it follows that when the parent rock presents with extremely high Cd content, the resulting soils will be contaminated, e.g., [16,21,23]. In our samples total Cd content was on average 50% lower in soils than in rocks, which is a typical range of decrease after weathering of the parent material, e.g., [16,21,38].

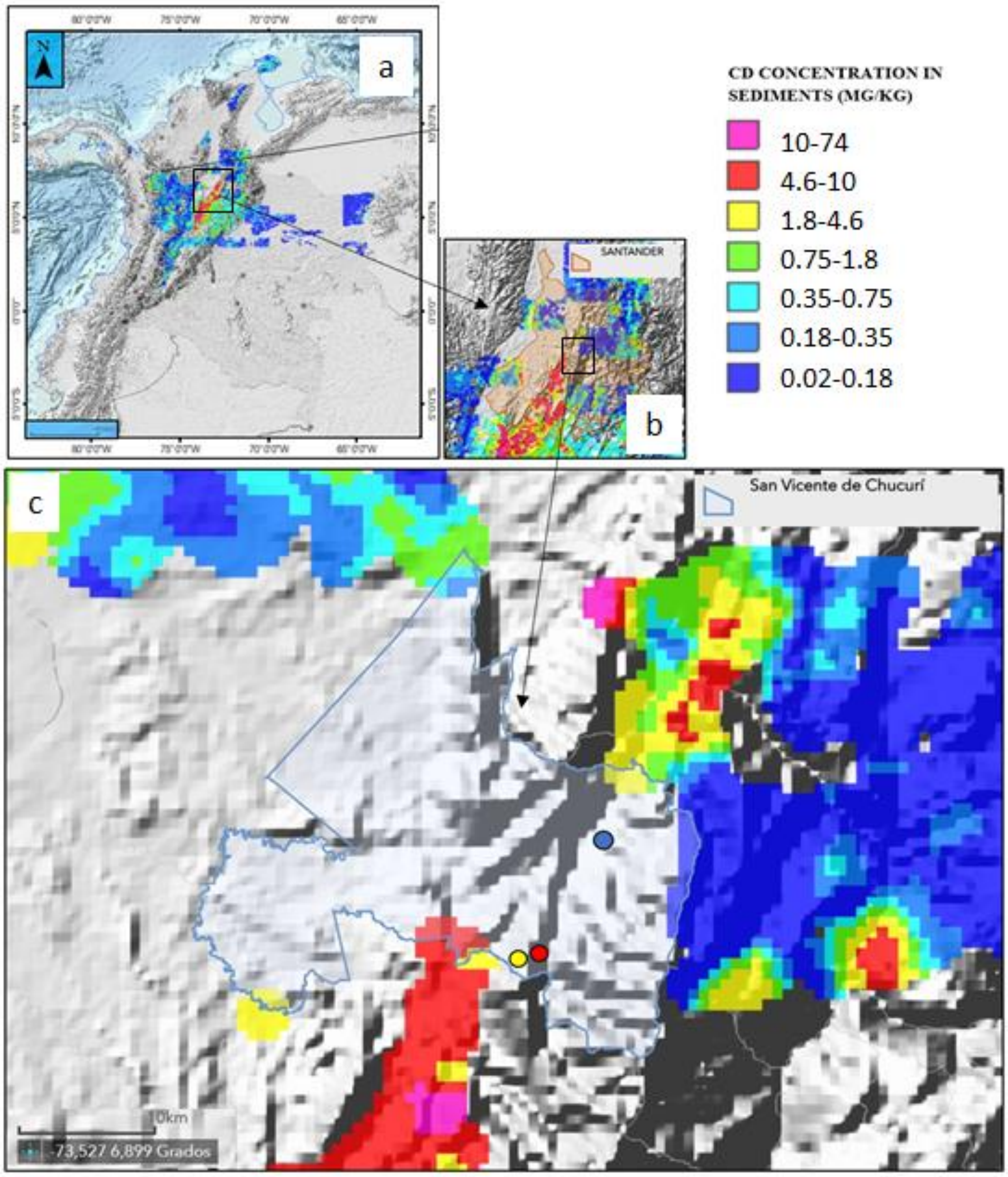

Figure 5. Map of cadmium content in sediments (mg/kg) in Colombia [39]. (**a**) Geochemical map of Cd for Colombia. (**b**) Geochemical map of Cd for Santander. (**c**) Geochemical map of Cd for San Vicente de Chucurí, Farm 1 (red dot), Farm 2 (yellow dot) and Farm 3 (blue dot) are indicated.

The soil samples studied have much higher average Cd concentrations (27 mg/kg $\pm$ 10.1) than those reported in other farms in San Vicente, which show an average of 3.3 mg/kg total Cd in soils, as well as mean values reported for soils in Santander and generally in Colombia [14,27]. Soil Cd concentrations in San Vicente de Chucurí are also much higher than international average Cd concentrations in cacao soils and well above the 1 mg/kg level usually found in soils (Figure 3; [9,27]). In fact, the measured values between 10 and 47 mg/kg in the soils studied fall within the range of typical polluted and metal-rich soils worldwide ([21] and references therein). While elevated Cd concentrations are not necessarily available for uptake and incorporation by the cacao plant, a correlation between geological substrate and Cd bioavailability and/or Cd content in cacao tissues has been previously reported in Colombia, e.g., [10]. Regardless of the specific values, it is clear that Cd in soils in the region is very elevated and represents a threat to cacao cultivation and commercialization, which is the basis of the local economy.

Of even more concern is that the vast majority of our samples do not comply with international regulations for tolerable values for mammals' exposure, ecosystems or critical thresholds for human health risks (Figure 3; [36,37]). Soils in the area also exceed the Ecological Soil Screening Levels set by the EPA (Eco-SSL) (0.36 mg/kg dry weight), which if surpassed is considered damaging to mammals and ecosystems [37]. This poses a serious health risk for people exposed to the soils and consuming crops in this particular area, as Cd accumulates in organisms and is potentially carcinogenic, as well as being linked to oxidative stress and kidney malfunction [1,21]. The values reported imply possible health issues, as Cd enters the human body through foods produced in soils that are contaminated with the metal, and after accumulation can cause poisoning or organ malfunction [20,21]. The farmers in the region also grow subsistence crops as well as raise animals for consumption, thus further increasing their exposure to the metal through bioaccumulation from consuming crops and animal products directly linked to the contaminated soils.

It is important to note that a high variability in concentrations of the metal at several scales has been reported [27] and is in fact observed within our study area (Figures 3 and 5; [14,27]). Total Cd concentrations in cacao soils from Santander range from 0.01 to 27 mg/kg, thus small-scale heterogeneity and/or additional Cd sources in our studied farms may be a variation factor [27]. Heterogeneity was previously reported, with farms in the east flank of the municipality having higher Cd averages than those in the west flank (Figure 5; [14]). Metal concentrations vary significantly within Farms 1 and 2, both smaller than 1 ha, suggesting that small-scale heterogeneity plays a significant role in Cd distribution, most likely coupled to the heterogeneous metal content in the parent material reported in the present study. Furthermore, additional sources of Cd may play a role, and will be discussed in the following sections.

It is crucial to consider that only about 4% of the total metal is in Cd^{2+} form, and hence bioavailable for plant uptake [6,8,14,15]. Therefore, we would expect to have about 1 mg/kg of available Cd in the study area (1.16 mg/kg in Farm 1; 1.04 mg/kg in Farm 2; and 1 mg/kg in Farm 3). This would be a reasonably standard level of Cd in soils were it not for the fact that the element bioaccumulates. Moreover, the high levels of Cd reported in nibs at the study area indicate a strong uptake and accumulation by the cacao plants (Figure 1).

4.2. Natural Cadmium Sources

Autochthonous sources are those intrinsic sources from which a component or element might be introduced into an ecosystem, area, or in this case, plantation. Cd has high mobility through sediment flows and erosion processes by water and wind, and material translocation, resulting in accumulation in sedimentary plains and rivers, e.g., [17]. High dependence of 'total' soil Cd has been linked to geological substrates, with the highest median concentration being found in alluvial sediments and soils developed on sedimentary rocks [20,25].

Our sampling sites are above the geological unit b6b6-Sm within the "Simití" formation that is made of laminated black claystones, carbonaceous and calcareous fine-grained rocks with calcareous concretions (Figure 2; [29,30]). This was confirmed by our petrographic analyses that indicated the presence of limestone, marl and shale in all our samples (Figure 4). All rocks analyzed are carbonaceous, thus they can hold substantial quantities of Cd by adhesion and absorption into pores (Figure 4; [40,41]). Calcite will bind Cd through cation exchanges due to the similar sizes and charges of Ca and Cd [7,8,40,41]. This is supported by the significant Pearson correlation between Cd and Ca in rocks (Pearson correlation = 0.79, $p < 0.05$), which points to the calcium-rich rocks as the main source of Cd in the present study, as has been seen in other studies [8,9,24].

Carbonate rocks with high Cd content, through the pedogenesis process, tend to produce soils enriched in the metal [24]. According to the petrographic analysis, the humic cambisols studied are mainly composed of unconsolidated carbonates and are rich in humus (Figure 4d). The abundance of carbonates is further confirmed by the ignition analysis of soils, which shows carbonates to range from 2.2 to 6.5 g (±0.1), consistent with soil forming from the underlying carbonate rocks. While the petrographic analysis confirms that soils in the area were formed by weathering of the carbonate-rich parental material rather than by transport of allochthonous material, no significant correlation is found between the Cd contents of rocks and soils. Such a strong association between parental material and Cd content in soils has been previously reported in other areas [20,21]. The lack of correlation for our dataset may be due to the heterogeneity of Cd concentrations in rocks as well as in weathering and pedogenesis processes.

Even though the carbonate rocks can have high Cd concentrations due to their porosity, it is strongly bound in their structure, which makes it less available for plant absorption. In fact, Ca addition has been used as a remediation strategy for high Cd concentrations in arable land as it binds the metal, e.g., [42,43].

The analyzed rocks also show the presence of Barite ($BaSO_4$), which has been found to be enriched with Cd, with levels of up to 9.9 mg/kg (Figure 4c; [41]). The Barite in parental rocks may further add Cd to the resulting soil after chemical weathering associated with pedogenesis.

4.3. Anthropogenic Cadmium Input

Fertilization, mining, construction sites and industrial activities that introduce extrinsic elements into the farm soils, as well as natural processes such as mass movements, water flows or aeolian deposition coming from Cd-rich areas, all constitute possible allochthonous sources [14,20,30]. Even though the region is known for hosting mining, there is no reported activity near the sampling area (confirmed by the farmers), which means that it can be ruled out as a significant source of Cd for the studied soils.

As we established that soils in the area are formed from the weathering of parental rock, mass movements, water and eolian transport can also be ruled out as significant Cd sources.

Another potential allochthonous source of the metal is fertilizer of sedimentary and phosphorous origin [44]. Approximately 85% of phosphate used in inorganic fertilizers is sourced from sedimentary deposits with high Cd levels [20,44,45]. Mineral fertilizers have been identified as the main source of Cd in some agricultural soils and organic waste-derived fertilizers have been shown to contribute metal content in some cases [44].

In the present study an inorganic fertilizer was used in Farm 2, but had only a marginally higher level of average concentrations compared to Farm 3 (where no fertilizer was used), which indicates a negligible effect on Cd soil content. In contrast, the organic fertilizer added in Farm 1 seems to slightly increase the average Cd soil concentration (Figure 3). Therefore, the organic fertilizer might be an additional source of Cd in the studied soils, which is a rare case since usually those types of fertilizers are less contaminating than chemical ones [44]. This was confirmed by the clustering of all the samples in Farm 1 when PCA was performed (Figure 6). We see that fertilizer had the strongest loading successfully separating Farm 1, where the organic fertilizer was applied, from the other two (Figure 6). This confirms the much stronger impact of the organic fertilization versus the inorganic one, which was already noted when comparing soil Cd concentrations (Figures 3 and 6).

The organic fertilizer applied to Farm 1 contained 64 ± 2 mg/kg Cd, well above the values for soils and most rock fragments measured in the area, and exceeding acceptable Cd levels for fertilizers in Europe (40 mg/kg; Figure 3; [45]). The organic fertilizer was sourced from chickens and pigs which were fed food residues and organic matter from crops grown in the same soils, clearly resulting in the biomagnification of Cd, and thus extremely high levels of the metal (Figure 3; [2,4]). This case is particularly worrisome since the Cd introduced with the fertilizer will be easily absorbed by the plants and result in further metal accumulation in cocoa beans.

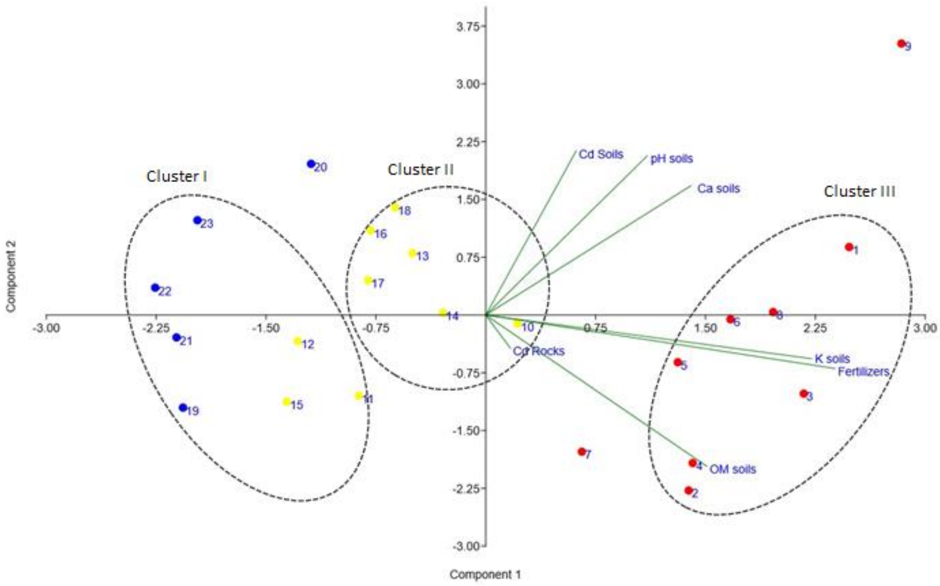

Figure 6. Principal component analysis including the main soil factors measured in the study soils. Clusters resulting from the paired-group analysis are overlaid. Farm 1 is indicated by red dots, Farm 2 by yellow dots and Farm 3 by blue dots; analysis carried out with PAST 4.07 [35].

In Farm 2, the inorganic fertilizer was used one year prior, but no addition was carried out close to the time of sampling. This could mean that part of the Cd added with the fertilizer may have already been removed from the soil, and that is why the average metal concentrations are the same as in the case of soils without fertilizer. Moreover, Cd concentrations measured in the inorganic fertilizer are below those measured in soil samples; thus, its addition would not be expected to raise metal concentrations significantly (Figure 3). We also see no clustering of Farms 2 and 3 related to the fertilizer variable (Figure 6). Despite the fact that Cd content in the inorganic fertilizer does not exceed the international legal limits, concentrations are still higher than the upper critical threshold; thus, it should not be used indiscriminately as it may cause Cd enrichment over time (Figure 3; [44]). Additionally, there is no guarantee that another batch of the same fertilizer might not have a much higher concentration of Cd, as lots tend to be heterogeneous due to production changes [44].

The metal can also be reintroduced into the soil through falling plant leaves or branches, and in some cases, farmers will leave plant debris as a fertilizer [8,9]. In all three plantations most of the organic matter falling from the cacao tree was left to degrade and decompose in situ; thus, the higher Cd concentration in top-soils (first 30 cm sampled) may in part be due to the accumulation of the metal over the years from leaves and husks. In farms in Central Colombia, cacao leaf litter has been found to have higher Cd content than both cacao beans and green leaves, with an average of 85.5 mg/kg, which implies a high level of Cadmium cycling [25,38]. This is supported by a study that coupled Cd concentrations and isotopes in cocoa soils indicating that the use of tree litter may indeed be an additional source of the element [46]. The use of vegetation waste originating within the same plantation as the fertilizer will recirculate bioavailable heavy metals, though the relative importance of this recycling process as a contributor to Cd accumulation in cacao beans is not yet fully understood. This may make the problem worse by re-introducing easily absorbable Cd^{2+} into the system, resulting in an enrichment of the element in the root area and enhanced uptake. This could be easily avoided by shifting to cultivation practices that recover waste away from the crops.

4.4. Soil Factors Affecting Cadmium Bioavailability

While soil Cd content is directly correlated with the bioavailability and cycling of the element in soils, not all the Cd present in soils will be available for uptake and incorporation. If the metal is either not bioavailable or irreversibly bound to the soil matrix, no transfer will take place [4]. In addition to the actual content of Cd in soils, several soil properties affect the Cd bioavailability and consequent root uptake [4]. High electrical conductivity and salinity concentrations, as well as loamy and clayey soil textures, result in higher Cd availability; fortunately, none of those are found in the soils of the study area. Indeed, most of the soil parameters including pH range, organic matter content or chemical composition result in reduced Cd availability [4,25].

Soils in humid tropical climates have been associated with the migration of Cd by leaching from the topsoil layer, which reduces concentrations in the cacao root area, e.g., [2,3]. However, we do not observe Cd leaching, which could be explained by the high slope of the cacao plantations we examined, which causes elevated run-off versus percolation, despite the humid climate. The lack of washing of surface soils may also be due to the pH range, carbonates and high organic matter, resulting in strong Cd binding [4,25].

The pH values of our soils ranged between 6 and 7.8 ($\pm$0.1), with little variation between farms and within the ideal range for retention of Cd within the soil matrix [4]. At pH higher than 5.5 the metal converts into insoluble carbonate and phosphate forms, making it unavailable [2,3]. Even when the soil pH is in the ideal range, Cd remobilization, absorption and accumulation in plant tissues may still occur as plants exude acids from their roots to improve the solubility of nutrients and ions, creating small acid pH zones where the metal can become available, e.g., [47]. For instance, Cd has been found to be a significant problem in cacao grown in near-neutral pH soils in the north of Peru and Honduras [9,48]. While microheterogeneity may partly explain Cd absorption in the present study, the high concentrations in beans are most likely linked to the extremely high levels of Cd in soils. Nonetheless, we observe that pH is one of the stronger loading variables in the PCA and is associated with the Cd in soils even though no significant linear correlation could be found between the two variables (Figure 6). In a study made in cacao systems in Ecuador, they reported that for pH values below 6.3 the beans can accumulate up to 8 times the Cd concentration found in soils, which would only be the case for two samples in our dataset (8.7%; [46]). Most of the data fall in the intermediate pH values (57%) with a predicted enrichment of 4-fold in the beans and the remaining 34.3% present a pH higher than 7 with only a 3.2 enrichment [46]. This would mean an averaged 4.1 enrichment factor for the beans in our farms. In fact, using the reported ratio of accumulation of 1:4 in soil to beans, and based on the highest Cd content of 9.34 mg/kg reported for beans, this would mean that only a maximum of 2.3 mg/kg of metal will be bioavailable in the soil for plant uptake [2,14,49]. Therefore, despite the extremely high reported values, the soil characteristics are significantly reducing the cacao plant uptake of Cd. Other studies in the area confirm the presence of Cd rich soils coupled with a lower proportion of the metal in the cacao tree structures [10,38].

While we find no correlation between Cd content in soils and manganese (Mn) or potassium (K), the PCA results show a strong loading of the K in the separation of cluster III (Figure 6). While the presence of both these elements may not alter the total Cd measured in soils, they have been shown to reduce plant Cd incorporation, probably due to ion competition [9,25]. As we were not able to measure the Cd content of beans, we cannot directly test this hypothesis. However, based on a ratio of 47.5 Mn to 1 Cd, well above the necessary 20 to 1, we assume that the presence of Mn in the studied soils will likely result in reduced Cd intake by plants [9,25]. We also find high K concentrations that work in a similar way, increasing ion competition and therefore decreasing Cd adsorption.

Organic soils have high sorption affinity for Cd: up to 30 times higher than mineral soils [2]. Soil OM will efficiently bind Cd^{2+}, especially if associated with pH levels between 5.5 and 7.5 [4]. Organic matter is known to have a significant surface area and micropores that can serve as sorption sites to retain humidity and nutrients, but also the positively charged Cd^{2+} [4]. The sampled soils had from 1.7 to 7 (±0.1) grams/kg of OM, with Farm 1 having the highest values (Figure 7). While data generally show the tendency, only Farm 1 showed a significant negative correlation with Cd content in soils (Figure 7). This may be because soils in Farm 1 have more bioavailable Cd, which is the one preferentially sequestered in OM. It may also be that due to factors such as salinity or more clay-rich textures, which were not considered in the present study, that will affect Cd presence and availability.

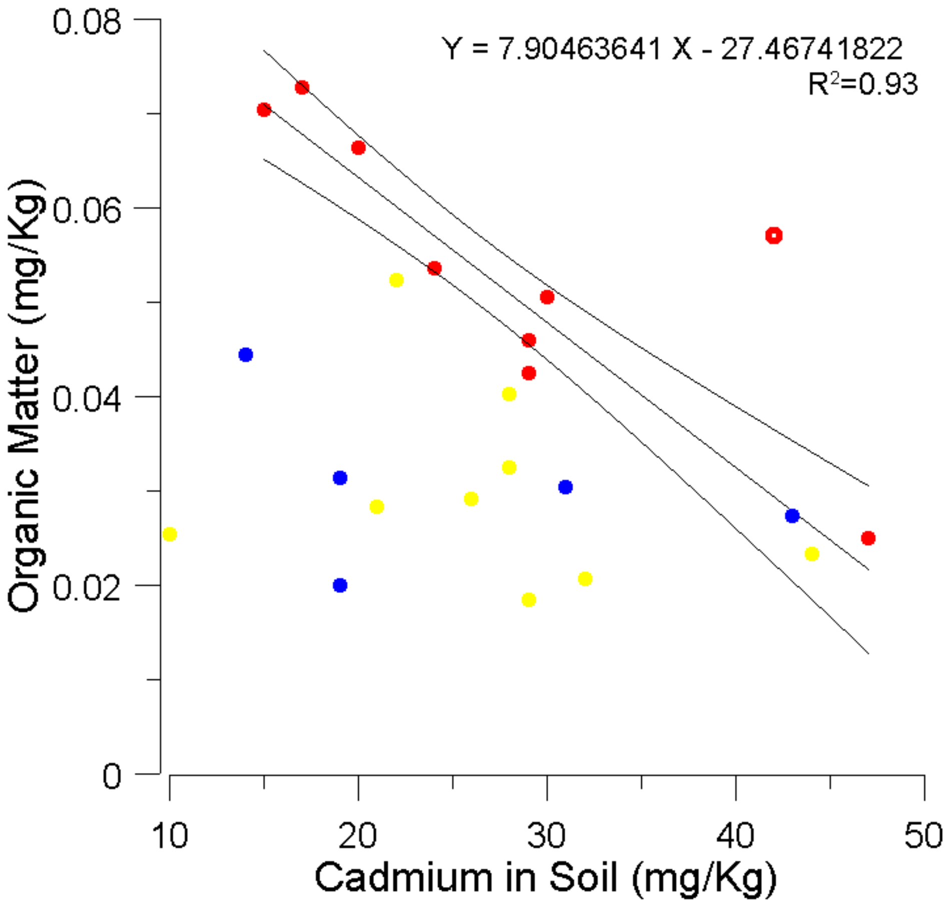

Figure 7. Correlation between cadmium in soils and organic matter content. Farm 1 is indicated in red, Farm 2 is indicated in yellow and Farm 3 is shown in blue. A linear fit has been added only for Farm 1 and the 95% confidence interval is shown; the void red dot has been excluded as an outlier.

Since factors such as the pH, organic matter content and the presence of carbonates mitigate the plant's uptake of the metal as they buffer and absorb the element, we conclude that the Cd availability is considerably below what it potentially could be, given the metal concentrations found in the area's soils. Without these mitigating soil characteristics, the exposure and availability of the metal would likely pose a much higher health risk and could mean even higher accumulation in cacao beans [1,4,21]. This would ultimately make them toxic and not suitable for consumption or commercialization.

The adsorption of Cd has also been reported for hematite and has been shown to be pH dependent with an exponential increase above pH values of 7 [50]. Our soils display an average pH of 6.9 and thus some of the Cd could be adsorbed into the hematite present (Figure 4c). However, this hypothesis could not be corroborated with the correlation between Fe and Cd, most likely because there are other iron sources besides hematite.

4.5. Suggested Mitigation Strategies

Solutions should be cost-effective and be a true aid for cacao farmers so that they can produce cacao beans with no or lower Cd values to sell to manufacturers, and potentially export. A Cd mitigation hierarchy approach should be implemented, by considering actions from farm to final product that are adapted to the specific conditions of the cacao value chain in question [14,48,51].

Eradicating the addition of organic fertilizers to minimize the amount of bioavailable Cd accumulation might be an easy and effective strategy [44] but, of course, a better approach would be to test fertilizers both chemical and organic in nature to guarantee that they have low metal values and can be applied as needed.

While the addition of soil amendments that alter pH, calcium or soil organic matter content to reduce the bioavailability of Cd for the cacao plants is widely used, it would not be useful in this particular case [8,52]. Amendments would not have an impact in the present study area since the soil parameters are already optimal for Cd sequestration.

Another potential solution is leaching, which can remove fertilizer and contaminant components over time [9]. The leaching or washing would move the Cd lower into the soil profile where the roots of the trees cannot uptake it (deeper than 100 cm) [53,54], stopping the accumulation in their structures. However, as we have seen, the chemical characteristics of the soils will strongly bind Cd to the matrix and prevent effective leaching of the element.

The selection of cacao species that are naturally low accumulators of Cd or with low Cd transfer from vegetative parts into the beans has high potential to keep Cd accumulation in cacao beans at levels that are safe for consumption [6]. However, this strategy can only be applied for new producers or for existing farms when they renovate their trees, and thus would have a limited impact in the study area.

Demineralization processes in cacao soils, linked to both biological and physical routes, are under consideration as solutions that would reduce the availability of the metal by its mineralization or biotransformation, e.g., [49–52]. Cadmium-tolerant bacteria (CdtB) and other microorganism existing in these Cd enriched cacao soils have been identified, with about 26 phylogenetically diverse bacteria (Actinobacteria, Alphaproteobacteria, Bacilli, Betaproteobacteria, Gammaproteobacteria) already described and under study for their biotransformation capabilities [8,50,52].

5. Conclusions

In all soil, rock and fertilizer samples in our study area, high levels of Cd were found, with the majority of them by far exceeding the limits set by international regulations.

The concentration of Cd in soils is determined by the geological substrate as an autochthonous source. The petrological analysis indicates the presence of Cd-bearing minerals and sedimentary rocks with high porosity that can hold Cd.

Fertilizers also showed a positive correlation with the Cd content in soils as the main allochthonous source, which can be managed with better practices. Testing fertilizers for heavy metals before their application should be a standard practice.

Even though the pH range, OM content and presence of Mn and K in the soils significantly diminish Cd bioavailability, there is still a high metal content in cocoa beans of the area.

We consider the selection of cacao species that are naturally low accumulators of Cd and the trial of microorganism with biotransformation and mineralization capabilities to be relatively fast and cost-effective solutions to the observed soil Cd enrichment.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/soilsystems7010012/s1, Table S1: Content of cadmium (Cd) for rocks and soils in mg/Kg. The error of the measurements is indicated (ε).

Author Contributions: For the present article the authors contributed as follows: Conceptualization, V.J.-B. and C.H.; methodology, V.J.-B. and C.H.; software, V.J.-B. and C.H.; validation, V.J.-B., C.H. and J.P.; formal analysis, V.J.-B., C.H. and J.P.; investigation, V.J.-B. and C.H.; resources, C.H. and J.P.;

data curation, V.J.-B. and C.H.; writing—original draft preparation, V.J.-B., C.H. and J.P.; writing—review and editing, V.J.-B., C.H. and J.P.; visualization, V.J.-B. and C.H.; supervision, C.H.; project administration, C.H.; funding acquisition, C.H. All authors have read and agreed to the published version of the manuscript.

Funding: The authors want to thank the Faculty of Science at the Universidad de los Andes for providing funding through project: INV-2019-84-1814 to CH.

Data Availability Statement: Data are available in the supplementary material.

Acknowledgments: We also want to acknowledge the countless hours spent by S. Salamanca perfecting the technique to produce soil thin sections.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Das, S.C.; Al-Naemi, H.A. Cadmium Toxicity: Oxidative Stress, Inflammation and Tissue Injury. *Occup. Dis. Environ. Med.* **2019**, *7*, 144–163. [CrossRef]
2. Kabata-Pendias, A.; Szteke, B. *Trace Elements in Abiotic and Biotic Environments*; Kabata-Pendias, A., Szteke, B., Eds.; Taylor & Francis: Boca Raton, FL, USA, 2015. [CrossRef]
3. Kabata-Pendias, A. *Trace Elements in Soils and Plants*, 4th ed.; Kabata-Pendias, A., Szteke, B., Eds.; CRC Press: Boca Raton, FL, USA, 2010. [CrossRef]
4. Mortensen, L.H.; Rønn, R.; Vestergård, M. Bioaccumulation of cadmium in soil organisms—With focus on wood ash application. *Ecotoxicol. Environ. Saf.* **2018**, *156*, 452–462. [CrossRef]
5. Nordberg, G.F. Historical perspectives on cadmium toxicology. *Toxicol. Appl. Pharmacol.* **2009**, *238*, 192–200. [CrossRef]
6. Engbersen, N.; Gramlich, A.; Lopez, M.; Schwarz, G.; Hattendorf, B.; Gutierrez, O.; Schulin, R. Cadmium accumulation and allocation in different cacao cultivars. *Sci. Total Environ.* **2019**, *678*, 660–670. [CrossRef]
7. Chavez, E.; He, Z.L.; Stoffella, P.J.; Mylavarapu, R.S.; Li, Y.C.; Moyano, B.; Baligar, V.C. Concentration of cadmium in cacao beans and its relationship with soil cadmium in southern Ecuador. *Sci. Total Environ.* **2015**, *533*, 205–214. [CrossRef]
8. Chavez, E.; He, Z.L.; Stoffella, P.J.; Mylavarapu, R.S.; Li, Y.C.; Baligar, V.C. Chemical speciation of cadmium: An approach to evaluate plant-available cadmium in Ecuadorian soils under cacao production. *Chemosphere* **2016**, *150*, 57–62. [CrossRef] [PubMed]
9. Argüello, D.; Chavez, E.; Lauryssen, F.; Vanderschueren, R.; Smolders, E.; Montalvo, D. Soil properties and agronomic factors affecting cadmium concentrations in cacao beans: A nationwide survey in Ecuador. *Sci. Total Environ.* **2019**, *649*, 120–127. [CrossRef]
10. Meter, A.; Atkinson, R.J.; Laliberte, B. *Cadmium in Cacao from Latin America and The Caribbean. A Review of Research and Potential Mitigation Solutions*; Development Bank of Latin America: Caracas, Venezuela, 2019; Available online: http://scioteca.caf.com/handle/123456789/1506 (accessed on 28 November 2022).
11. The European Commission. Commission Regulation (EU) no 488/2014 of 12 may 2014 amending regulation (EC) no 1881/2006 as regards maximum levels of cadmium in foodstuffs. *Off. J. Eur. Union* **2014**, *488*, 75–79.
12. Abbott, P.C.; Benjamin, T.J.; Burniske, G.R.; Croft, M.M.; Fenton, M.; Kelly, C.R.; Lundy, M.; Camayo, F.R.; Wilcox, M.D. An Analysis of the Supply Chain of Cacao in Colombia. Technical Report. In Purdue University International Center for Tropical Agriculture (CIAT). 2018. Available online: https://pdf.usaid.gov/pdf_docs/PA00W4KG.pdf (accessed on 27 November 2022).
13. Fernández-Niño, M.; Rodríguez-Cubillos, M.J.; Herrera-Rocha, F.; Anzola, J.M.; Cepeda-Hernández, M.L.; Mejía, J.L.A.; Chica, M.J.; Olarte, H.H.; Rodríguez-López, C.; Calderón, D.; et al. Dissecting industrial fermentations of fine flavour cocoa through metagenomic analysis. *Sci. Rep.* **2021**, *11*, 8638. [CrossRef] [PubMed]
14. de Walque, B.; Boeckx, P.; Dewettinck, K. Biophysical Control on Cocoa Quality in Santander, Colombia, 2017–2018. Ph.D. Thesis, Univeristy of Ghent, Ghent, Belgium, August 2018. Available online: https://lib.ugent.be/fulltxt/RUG01/002/509/472/RUG01-002509472_2018_0001_AC.pdf (accessed on 28 November 2022).
15. Smolders, E. Cadmium uptake by plants. *Int. J. Occup. Med. Environ. Health* **2001**, *14*, 177–183. [PubMed]
16. Liu, Y.; Xiao, T.; Perkins, R.B.; Zhu, J.; Zhu, Z.; Xiong, Y.; Ning, Z. Geogenic cadmium pollution and potential health risks, with emphasis on black shale. *J. Geochem. Explor.* **2017**, *176*, 42–49. [CrossRef]
17. Aflizar; Aprisal; Alarima, C.I.; Masunaga, T. Effect of soil erosion and topography on distribution of cadmium (Cd) in Sumani watershed, west Sumatra, Indonesia. *MATEC Web Conf.* **2018**, *229*, 03001. [CrossRef]
18. Page, A.L.; Chang, A.C.; El-Amamy, M. Cadmium levels in soils and crops in the United States. In *Lead, Mercury, Cadmium and Arsenic in the Environment*; John Wiley and Sons: New York, NY, USA, 1987; pp. 119–146.
19. Carrillo-González, R.; Šimůnek, J.; Sauvé, S.; Adriano, D. Mechanisms and pathways of trace element mobility in soils. *Adv. Agron.* **2006**, *91*, 111–178.
20. Smolders, E.; Mertens, J. Cadmium. In *Heavy Metals in Soils: Trace Metals and Metalloids in Soils and Their Bioavailability*; Alloway, B.J., Ed.; Springer Science & Business Media: Berlin/Heidelberg, Germany, 2013; Volume 22, pp. 283–312.

21. He, S.; He, Z.; Yang, X.; Stoffella, P.J.; Baligar, V.C. Soil biogeochemistry, plant physiology, and phytoremediation of cadmium-contaminated soils. *Adv. Agron.* **2015**, *134*, 135–225.
22. Marowsky, G.; Wedepohl, K.H. General trends in the behavior of Cd, Hg, Tl and Bi in some major rock forming processes. *Geochim. Cosmochim. Acta* **1971**, *35*, 1255–1267. [CrossRef]
23. Johnson, D.L.; Watson-Stegner, D. Evolution model of pedogenesis. *Soil Sci.* **1987**, *143*, 349–366. [CrossRef]
24. Xia, X.; Ji, J.; Yang, Z.; Han, H.; Huang, C.; Li, Y.; Zhang, W. Cadmium risk in the soil-plant system caused by weathering of carbonate bedrock. *Chemosphere* **2020**, *254*, 126799. [CrossRef]
25. Gramlich, A.; Tandy, S.; Gauggel, C.; López, M.; Perla, D.; Gonzalez, V.; Schulin, R. Soil cadmium uptake by cocoa in Honduras. *Sci. Total Environ.* **2018**, *612*, 370–378. [CrossRef] [PubMed]
26. Federación Nacional de Cacaoteros. Available online: https://www.fedecacao.com.co/ (accessed on 10 October 2022).
27. Bravo, D.; Leon-Moreno, C.; Martínez, C.A.; Varón-Ramírez, V.M.; Araujo-Carrillo, G.A.; Vargas, R.; Quiroga-Mateus, R.; Zamora, A.; Rodríguez, E.A.G. The First National Survey of Cadmium in Cacao Farm Soil in Colombia. *Agronomy* **2021**, *11*, 761. [CrossRef]
28. Vanderschueren, R.; Argüello, D.; Blommaert, H.; Montalvo, D.; Barraza, F.; Maurice, L.; Schreck, E.; Schulin, R.; Lewis, C.; Vazquez, J.L.; et al. Mitigating the level of cadmium in cacao products: Reviewing the transfer of cadmium from soil to chocolate bar. *Sci. Total Environ.* **2021**, *781*, 146779. [CrossRef]
29. Moreno, G.; Sarmiento, G. Estratigrafía Cuantitativa de las Formaciones Tablazo y Simití en las localidades de Sáchica (Boyacá) y Barichara—San Gil (Santander), Colombia. *Geología Colomb.* **2002**, *27*, 51–74.
30. Gómez, J.; Nivia, Á.; Montes, N.E.; Almanza, M.F.; Alcárcel, F.A.; Madrid, C.A. *Notas Explicativas: Mapa Geológico de Colombia*; Gómez, J., Almanza, M.F., Eds.; Compilando la geología de Colombia: Una visión a 2015. Servicio Geológico Colombiano; Publicaciones Geológicas Especiales: Bogotá, Colombia, 2015; pp. 9–33.
31. Nelson, D.W.; Sommers, L.E. Total carbon, organic carbon, and organic matter. In *Methods of Soil Analysis: Part 2 Chemical and Microbiological Properties*; Page, A.L., Ed.; Soil Science Society of America and American Society of Agronomy: Madison, WI, USA, 1983; pp. 539–579. [CrossRef]
32. Oxford Instruments Ltd. Manual de operador X-MET 7500. Industrial Analysis. 2012. Available online: https://fccid.io/ANATEL/02758-12-08305/Manual-X-MET-7500/B28832EF-BF4A-4C25-817D-C8675B600D4E (accessed on 1 October 2022).
33. Imanishi, Y.; Bando, A.; Komatani, S.; Wada, S.I.; Tsuji, K. Experimental parameters for XRF analysis of soils. *Powder Diffr.* **2010**, *53*, 248–255.
34. Bortolotti, M.; Lutterotti, L.; Pepponi, G. Combining XRD and XRF analysis in one Rietveld-like fitting. *Powder Diffr.* **2017**, *32*, S225–S230. [CrossRef]
35. Hammer, Ø.; Harper, D.A.; Ryan, P.D. PAST: Paleontological statistics software package for education and data analysis. *Palaeo Electron.* **2001**, *4*, 9.
36. Brus, D.J.; de Gruijter, J.J.; Walvoort, D.J.J.; de Vries, F.; Bronswijk, J.J.B.; Römkens, P.F.A.M.; de Vries, W. Mapping the Probability of Exceeding Critical Thresholds for Cadmium Concentrations in Soils in the Netherlands. *J. Environ. Qual.* **2002**, *31*, 1875–1884. [CrossRef]
37. United States Environmental Protection Agency. Regional Screening Levels (RSLs)—User's Guide. Available online: https://www.epa.gov/risk/regional-screening-levels-rsls-users-guide (accessed on 10 October 2022).
38. Albarrcín, H.S.R.; Contreras, A.E.D.; Henao, M.C. Spatial regression modeling of soils with high cadmium content in a cocoa producing area of Central Colombia. *Geoderma Reg.* **2019**, *16*, e00214. [CrossRef]
39. Atlas Geoquímico de Colombia. Available online: https://srvags.sgc.gov.co/JSViewer/Atlas_geoquimico_2018/ (accessed on 10 October 2022).
40. Shirvani, M.; Kalbasi, M.; Shariatmadari, H.; Nourbakhsh, F.; Najafi, B. Sorption—desorption of cadmium in aqueous palygorskite, sepiolite, and calcite suspensions: Isotherm hysteresis. *Chemosphere* **2006**, *65*, 2178–2184. [CrossRef]
41. Pivovarov, S. Adsorption of cadmium onto hematite: Temperature dependence. *J. Colloid Interface Sci.* **2001**, *234*, 1–8. [CrossRef]
42. Lu, Q.; Xu, Z.; Xu, X.; Liu, L.; Liang, L.; Chen, Z.; Dong, X.; Li, C.; Wang, Y.; Qiu, G. Cadmium contamination in a soil-rice system and the associated health risk: An addressing concern caused by barium mining. *Ecotoxicol. Environ. Saf.* **2019**, *183*, 109590. [CrossRef]
43. Marini, M.; Caro, D.; Thomsen, M. The new fertilizer regulation: A starting point for cadmium control in European arable soils? *Sci. Total Environ.* **2020**, *745*, 140876. [CrossRef] [PubMed]
44. Roberts, T.L. Cadmium and phosphorous fertilizers: The issues and the science. *Procedia Eng.* **2014**, *83*, 52–59. [CrossRef]
45. News European Parliament. Available online: https://www.europarl.europa.eu/news/en/press-room/20181119IPR19407/fertilisers-cadmium-parliament-and-council-negotiators-reach-provisional-deal (accessed on 10 October 2022).
46. Barraza, F.; Moore, R.E.T.; Rehkämper, M.; Schreck, E.; Lefeuvre, G.; Kreissig, K.; Coles, B.J.; Maurice, L. Cadmium isotope fractionation in the soil–cacao systems of Ecuador: A pilot field study. *RSC Adv.* **2019**, *9*, 34011–34022. [CrossRef]
47. Dong, J.; Mao, W.H.; Zhang, G.P.; Wu, F.B.; Cai, Y. Root excretion and plant tolerance to cadmium toxicity—A review. *Plant Soil Environ.* **2007**, *53*, 193–200. [CrossRef]
48. Zug, K.L.M.; Yupanqui, H.A.H.; Meyberg, F.; Cierjacks, J.S.; Cierjacks, A. Cadmium Accumulation in Peruvian Cacao (Theobroma cacao L.) and Opportunities for Mitigation. *Water Air Soil Pollut.* **2019**, *230*, 72. [CrossRef]
49. Khan, M.A.; Khan, S.; Khan, A.; Alam, M. Soil contamination with cadmium, consequences and remediation using organic amendments. *Sci. Total Environ.* **2017**, *601–602*, 1591–1605. [CrossRef]

50. Topcu, A.; Bulat, T. Removal of cadmium and lead from aqueous solution by Enterococcus faecium strains. *J. Food Sci.* **2010**, *75*, 13–17. [CrossRef] [PubMed]
51. Bravo, D.; Pardo-Díaz, S.; Benavides-Erazo, J.; Rengifo-Estrada, G.; Braissant, O.; Leon-Moreno, C. Cadmium and cadmium-tolerant soil bacteria in cacao crops from northeastern Colombia. *J. Appl. Microbiol.* **2018**, *124*, 1175–1194. [CrossRef] [PubMed]
52. Liu, J.; Hue, N.V. Amending subsoil acidity by surface applications of gypsum, lime, and composts. *Commun. Soil Sci. Plant Anal.* **2001**, *32*, 2117–2132. [CrossRef]
53. Dermont, G.; Bergeron, M.; Mercier, G.; Richer-Laflèche, M. Soil washing for metal removal: A review of physical/chemical technologies and field applications. *J. Hazard. Mater.* **2008**, *152*, 1–31. [CrossRef]
54. Torres, L.G.; Lopez, R.B.; Beltran, M. Removal of As, Cd, Cu, Ni, Pb, and Zn from a highly contaminated industrial soil using surfactant enhanced soil washing. *Phys. Chem. Earth* **2012**, *37–39*, 30–36. [CrossRef]