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

Valentina Joya-Barrero
Universidad de Los Andes
Carme Huguet (drhuguet@gmail.com)
Universidad de Los Andes https://orcid.org/0000-0001-8025-2010
Jillian Pearse
Universidad de Los Andes

Research Article

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Natural and anthropogenic sources of cadmium in cacao crop soils in Santander, Colombia

Valentina Joya-Barrero[1], Carme Huguet[1]* (0000-0001-8025-2010), Jillian Pearse[1] (0000-0002-7805-2244)

[1] Department of Geosciences, Los Andes University, Bogota, Colombia

Abstract

Cadmium (Cd) levels in cacao products from Santander, the main producing area in Colombia, are well above those permitted for export of cocoa products and may pose a potential health hazard. High Cd in cacao is related to the high content of the metal in beans, which in turn is linked to high concentrations of Cd in soils. Geochemical and petrographic analyses of fertilizer, soil and rock samples from three farms were carried out to determine the sources of Cd and soil characteristics that can affect its bioavailability, in order to identify strategies that may reduce Cd in cocoa. Autochthonous natural sources determine the Cd concentration in soils, with a high correlation between elevated Cd in sedimentary parental rocks and soil metal levels. While no industrial or mining inputs were present, an organic fertilizer was identified as a great allochthonous source of Cd in soils. High levels in the fertilizer were probably due to bioaccumulation of the element, since it was sourced from animals in the same area. The addition of crop waste to fertilize the soil may further contribute bioavailable Cd. Even though the pH range, high OM content and presence of Mn and K all diminish bioavailability, the high metal content in the farm soils still results in significant uptake by the cocoa plants and accumulation in the beans. We suggest that phytoremediation and biological amendments, as well as testing of fertilizers before application, could all be cost-effective solutions to reduce Cd levels in the final product.

Key Words: Cadmium, Cacao, Soil analysis, Autochthonous origin of Cd, Allochthonous origin of Cd.

*Corresponding author: m.huguet@unaindes.edu.co

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Author contributions:

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Valentina Joya-Barrero, and Carme Huguet. The first draft of the manuscript was written by Valentina Joya-Barrero and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Data inclusion:

Since the collected data are identified with specific farms authors will refrain form including the data in the initial submission. Authors are happy to include their data as supplementary material once the paper is published.

1. Introduction

Cadmium (Cd) is a non-essential heavy metal that can cause toxic effects in plants, animals and humans even at low concentrations (e.g. Kabata-Pendias 2010; Kabata-Pendias and Szteke, 2015). Because of its mobility in soils, it is readily absorbed by plants despite not having a metabolic function (Benavides et al., 2005). As the metal does not biodegrade, it bioaccumulates through the food web eventually posing a health hazard for humans (e.g. Kabata-Pendias and Szteke, 2015; Mortensen et al., 2018). Cd is considered to be one of the most toxic metals: it exhibits adverse effects on all biological processes, acting as a precursor of various cancers, oxidative stress, and kidney malfunction (e.g. KabataPendias and Szteke, 2015). Chocolate and cacao powder with elevated Cd levels may be an important source of human exposure to the metal (e.g. Engbersen et al., 2019).

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 cocoa-producing countries (Chavez et al., 2015, 2016; Argüello et al., 2019; Meter et al., 2019). Latin America and the Caribbean show high Cd content in cacao beans with mean values of the metal being above the acceptable limit (Fig. 1A; Chavez et al., 2015, 2016; Argüello et al., 2019; Meter et al., 2019). Moreover, starting in January 2020, the European Union enforced a new regulation of the maximum values for Cd concentrations in cocoa-based products, which has put a strain on South and Central American cacao producers (The European Commission, 2014).

Colombia is one of the world's major cacao producers, contributing 1.5% of the global market (e.g. Abbott , 2018). Santander is a well-known cacao region in Colombia, historically recognized for having vast areas of cacao crops (62,500 Ha) of excellent quality (e.g. Fernández-Niño et al., 2021). Recently, cacao has been highlighted, in the context of post-conflict in Colombia, as the main substitution crop for coca plantations, with 25,000 Ha having already been transformed from illegal crops into cacao (Fernández-Niño et al., 2021). 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 (Federación Nacional de Cacaoteros, 2020).

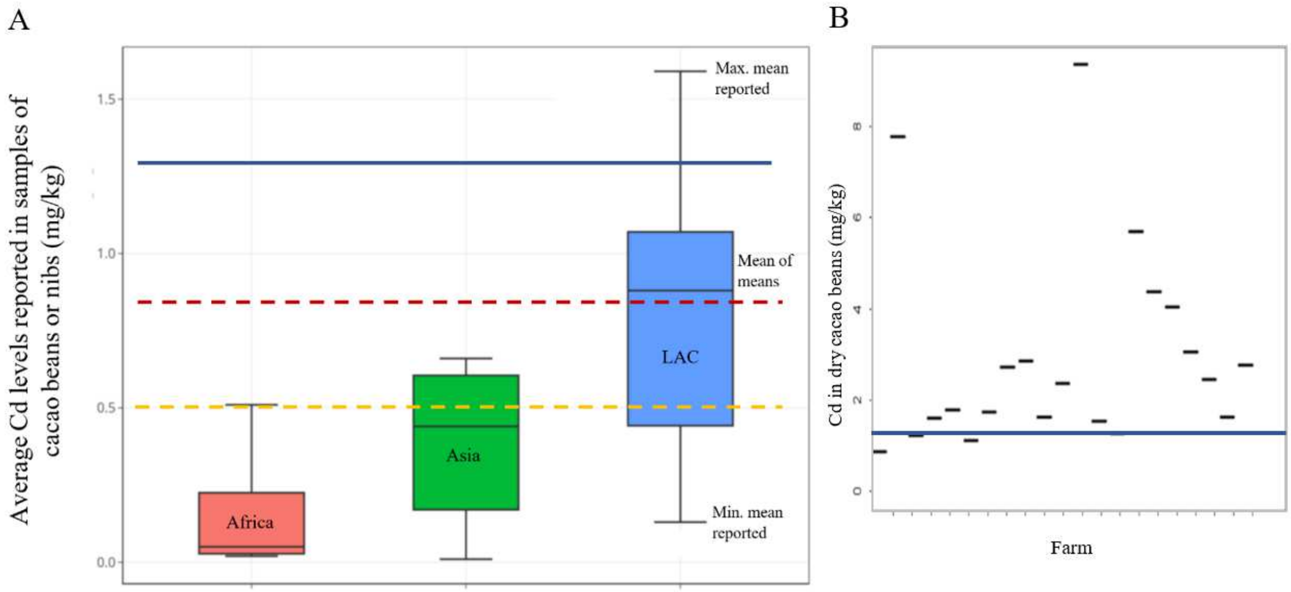

Figure 1. Cadmium levels in cacao beans. A) Average Cd levels reported in samples of cacao beans or nibs from three different continents: Africa, Asia and LAC-Latin America and the Caribbean (Meter et. al., 2019), overlaid: the ideal maximum level of 0.5 mg/kg (yellow dashed line), the acceptable limit in beans of 0.8 mg/kg (red dashed 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 Contaminant in Food (solid blue line), all limits as described by de Walque (2018); Figure adapted from Figure 2. in Meter et. al. (2019). B) Cd content in dry cacao beans from 21 farms located in San Vicente de Chucurí, Santander against the same maximum limit of 1.3 mg/kg shown in panel A (solid blue line); Figure adapted from original Figure 4.28 in de Walque (2018).

The *Theobroma cacao* plant is a bioaccumulator of Cadmium (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. Smolders, 2001;Chavez et al., 2016; Engbersen et al., 2019). The accumulation occurs preferentially in cacao beans, followed by fruit shells, and the smallest quantity of the metal accumulates in leaves (Chavez et al., 2015; Khan et al., 2017; Engbersen et al., 2019). 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 may vary, there is always substantial accumulation in beans (Chavez et al., 2015; Khan et al., 2017; Engbersen et al., 2019).

Even though other forms of Cd co-exist with the Cd^{2+}, contributing to the total content of the metal in the bedrock and soil, only the ion is available for plant uptake (Smolders, 2001; Chavez et al., 2016; Engbersen et al., 2019). The parental rock and the demineralization and weathering processes during pedogenesis will determine the amount of bioavailable Cd^{2+} (e.g. Johnson & Watson-Stegner, 1987; Duchaufour, 2012). 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 (Xia et al., 2020). Furthermore, several soil properties regulate Cd bioavailability: high electrical conductivity and salinity as well as loamy and clayey soil textures result in higher Cd availability, while near neutral pH range, organic matter content or presence of certain elements reduce its availability (Gramlich et al., 2018; Mortensen et al., 2018).

Previous studies show that concentration of Cd in plant structures can vary depending on the farm location and the soil characteristics (e.g. He et al., 2015; Argüello et al., 2019). 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 (Argüello et al., 2019; Bravo et al. 2021). Santander shows the second highest Cd soil concentration, with a mean of 1.90 mg/kg and a maximum value of 27mg/kg Cd — well above those of other regions in the country (Bravo et al. 2021). Perhaps not surprisingly, average Cd concentrations as high has 3.3 mg/kg for beans have been reported in the area (Fig. 1B; de Walque et al., 2018), far exceeding the safe level of 1.3 mg/kg established by The European Union Regulating Commission (Fig. 1B; de Walque et al., 2018; The European Commission, 2014).

Cadmium can originate from bedrock, erosional-depositional and recycling processes as well as from anthropogenic sources (Aflizar et al., 2018; Liu et al., 2017; Smolders, 2001). 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 (Page et al., 1987; Aflizar et al., 2018). Concentrations of cadmium are higher in sedimentary rocks since this metal can be easily adsorbed into fine particles and porosity sites, which are common to several rocks of this kind (Carrillo-González et al., 2003; Liu et al., 2017). The Cd content tends to be higher in fine grained acidic sedimentary rocks (He & al., 2015; Smolders & Mertens, 2013; Liu et al., 2017). The relative accumulation of Cd in sedimentary environments is also caused by the degassing of the Earth and mantle processes, in which the excess of volatile elements such as Cd is liberated and accumulated within empty spaces in sedimentary rocks (Marowsky & Wedepohl, 1971).

The anthropogenic sources of Cd are mainly related to the addition of both organic and inorganic fertilizers, and to the potential contamination from mining or construction sites (e.g. Smolders & Mertens, 2013). Cd can also be reinserted into the soil through the falling of the plant's leaves or branches, and in some cases, farmers will leave plant debris as a fertilizer, thus recycling the metal into the ground (e.g. Argüello et al., 2019; Engbersen et al., 2019).

Our aim is to improve the understanding of the possible allochthonous and autochthonous sources of the metal in the study area. We also analyzed soil parameters that may regulate the bioavailability of the metal. Providing a sound baseline of Cd levels and sources sinks is a first step towards better management practices and when needed, remediation strategies.

2. Materials and Methods

2.1. Study area

San Vicente de Chucurí is located in the Northeastern region of the department of Santander, Colombia (Fig. 2) and it is known as the "cocoa capital of Colombia" (Fig. 2). The annual mean temperature is 23.7 °C and average annual rainfall is 1820 mm (de Walque et al., 2018) 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 the high altitudes (900-1200 m.a.s.l.) (de Walque et al., 2018). All the study sites fall in the CMu soils category, with some soil differentiation and the inclusion 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, carbonaceous and locally calcareous fine-grained rocks, and the presence of calcareous concretions is significant (Fig. 2; Moreno & Sarmiento, 2002).

There is a noticeable enrichment of the metal in the west flank of the Eastern Andean Cordillera corresponding to territories within the departments of Santander, Boyacá and Cundinamarca (Fig. 3). Even though the study farms are within an area with no reported 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 (Fig. 3). 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 have a maximum of around 2.5 mg/kg total and 0.1 mg/kg of available Cd (de Walque et al., 2018).

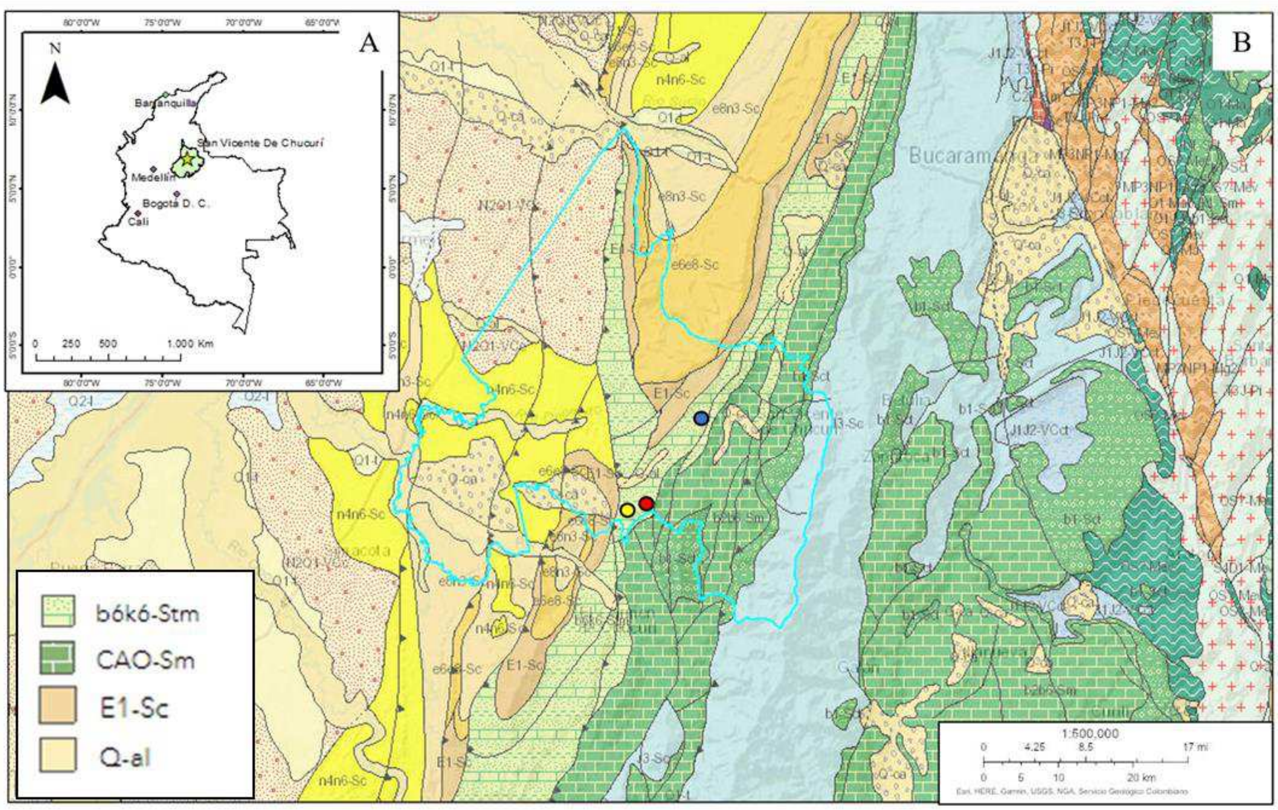

Figure 2. Maps of the study area. A) Map of Colombia with the country´s main cities. The department of Santander is highlighted in green with a star indicating the location of San Vicente de Chucurí. B) Geological map of San Vicente de Chucurí (Gomez et al., 2015): the light blue line delimits the municipality. 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 soil, 12 source rock and 2 fertilizers) were collected and analyzed at three different farms in the study area. An organic fertilizer was used in Farm 1 and an inorganic one in Farm 2; no fertilizer was added at Farm 3. In Farms 1 and 2, which are plantations of less than 1 Ha, the sampling was done in transects. 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. No rock samples were collected in this case since soil was homogenized in the first 2 meters 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 30µm 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. Mineral chemical composition was established using a scanning electron microscope (SEM). Back-scattered Electro (BSE) and X-ray spectroscopy (EDS) images were obtained using a Hitachi microscope, model S3000N at an accelerating voltage of 20 kV.

2.4 Soil analysis

A LAQUAact-PC110 probe was used to measure the pH in soil samples. To do so, 1g of humid soil was placed in 9 ml of distilled water and the solution was mixed for 2 minutes 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.

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 hours. Samples were then weighted and the difference in mass was assumed as combusted OM.

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

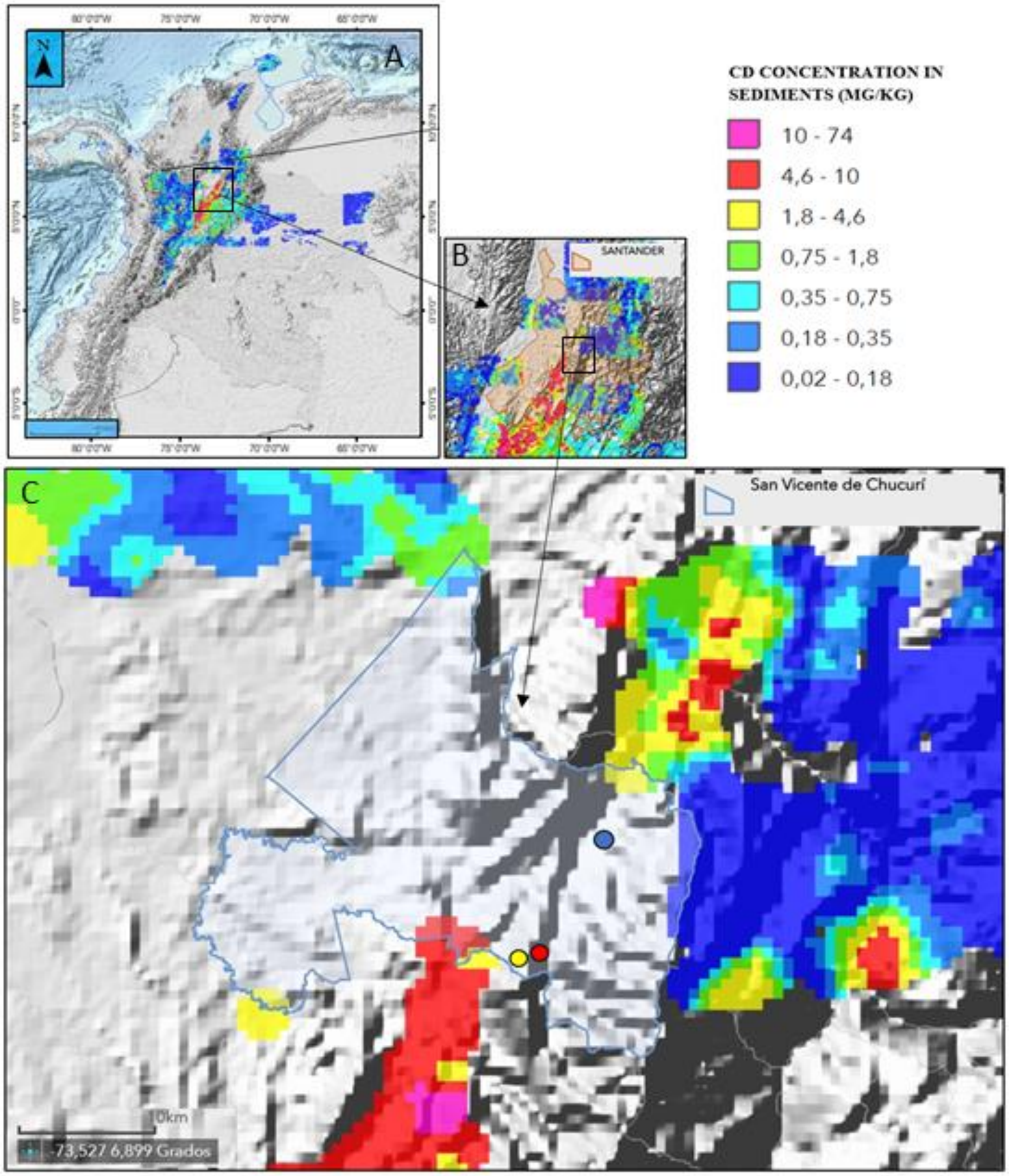

Figure 2. Map of Cd Content in Sediments (mg/kg) in Colombia and in the study area (http://srvags.sgc.gov.co/JSViewer/Atlas_geoquimico_2018/). A) Geochemical map of Colombia. B) Geochemical map of Santander. C) Geochemical map of San Vicente de Chucurí, in which Farm 1 is indicated by the red dot; Farm 2 is indicated by the yellow dot; and Farm 3 is indicated by the blue dot.

2.5 X-Ray Fluorescence (XRF) measurements

Element composition was measured in the soil and rock samples. For soils, 250 gr 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 (Imanishi et al., 2010). 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 ~2g of soil. This was done in order to minimize measurement variation due to soil heterogeneity. 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.

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. Imanishi et al., 2010; Bortolotti et al., 2017). For the rock samples the error is generally larger, probably caused by performing the measurement 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 (Fig. 4, Imanishi et al., 2010; Oxford Instruments Ltd., 2012).

3. Results and 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 the national production. Addressing elevated Cd content is crucial not only as a public health concern, but also for the potentially negative impact it could have on cacao exports, a key economic sector for the region (Jimenéz Tobón, 2015; Federación Nacional de Cacaoteros, 2019). Cadmium can be of autochthonous and/or allochthonous origin: sources include bedrock, erosional-depositional and recycling processes as well as anthropogenic input, and several soil properties regulate its bioavailability (Smolders, 2001; Gramlich et al., 2018; Mortensen et al., 2018; Engbersen et al., 2019). 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.

3.1. Cadmium levels in the study area

All the samples analyzed show elevated Cd values compared to both international standards and national averages (Figs. 1 and 4; Bravo et al., 2021). In fact, the entire left flank of the Colombian western 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 (Fig. 3).

The parental rock in the study area presents unusually high Cd concentrations with values of up to 3 times higher than previously reported in central Colombia (Rodríguez Albarracín et al., 2019). The highest value (90 mg/kg) was found in a rock fragment collected in Farm 1, at double the average Cd concentration of all other rock samples (45 mg/kg; Fig. 4). Previously reported anomalously high Cd levels in rocks range between 8.15 mg/kg and 21.4 mg kg worldwide (He et al., 2015 and references therein), confirming the extremely elevated Cd concentrations of the area rocks. Rock Cd values in the studied farms, even though always unusually elevated, vary from 30 to 50 mg/km, suggesting heterogeneity of the parent material's metal content (Fig. 4).

Total Cd content in cacao soils has been found to be mainly present as residual and oxidable fractions, associated with the meteorization of the bedrock and pedogenesis, so when the parental rock presents extremely high Cd content, it results in the formation of contaminated soils (e.g. Johnson & Watson-Stegner, 1987; Duchaufour, 2012; He et al., 2015; Liu et al., 2017). In our samples total Cd content was on average 50% lower in soils (27 mg/kg) than in rocks (52.6 mg/Kg), which is a typical range of decrease after weathering of the parent material (e.g. He et al., 2015; Liu et al., 2017; Rodríguez Albarracín et al., 2019). Our values are much higher than those reported in other farms in San Vicente, which show an average of 3.3 mg/kg total Cd (de Walque et al., 2018), as well as mean values reported for soils in Santander and generally in Colombia (Bravo et al., 2021). 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 (Figs. 1 and 4; Argüello et al., 2019). In fact, the measuured values between 10 and 47 mg/kg in the soils studied, fall within the range of typical values for polluted and metal-rich soils worldwide (He et al., 2015 and references therein). 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 economies of these municipalities.

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 (Fig.

5; Brus et al., 2002; United States Environmental Protection Agency, 2019). 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 (United States Environmental Protection Agency, 2019). This would pose 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 even at low concentrations (He et al., 2015). 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 (Smolders & Mertens, 2013; He et al., 2015). The farmers in the region also grow subsistence crops such as yuca and banana, thus further increasing their exposure to the metal. 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. Gramlich et al., 2018; Mortensen et al., 2018; Meter et al., 2019).

It is important to note that a high variability in concentrations of the metal at several scales has been reported (Argüello et al., 2019) and in fact is observed within our study area (de Walque et al., 2018; Bravo et al., 2021). 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 factor (Bravo et al., 2021). Heterogeneity was previously reported, with farms in the east flank of the municipality having higher Cd averages than those in the west flank (de Walque et al., 2018). 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 heterogeneous metal content in the parent material. Furthermore, additional sources of Cd may play a role, and will be discussed in the following sections.

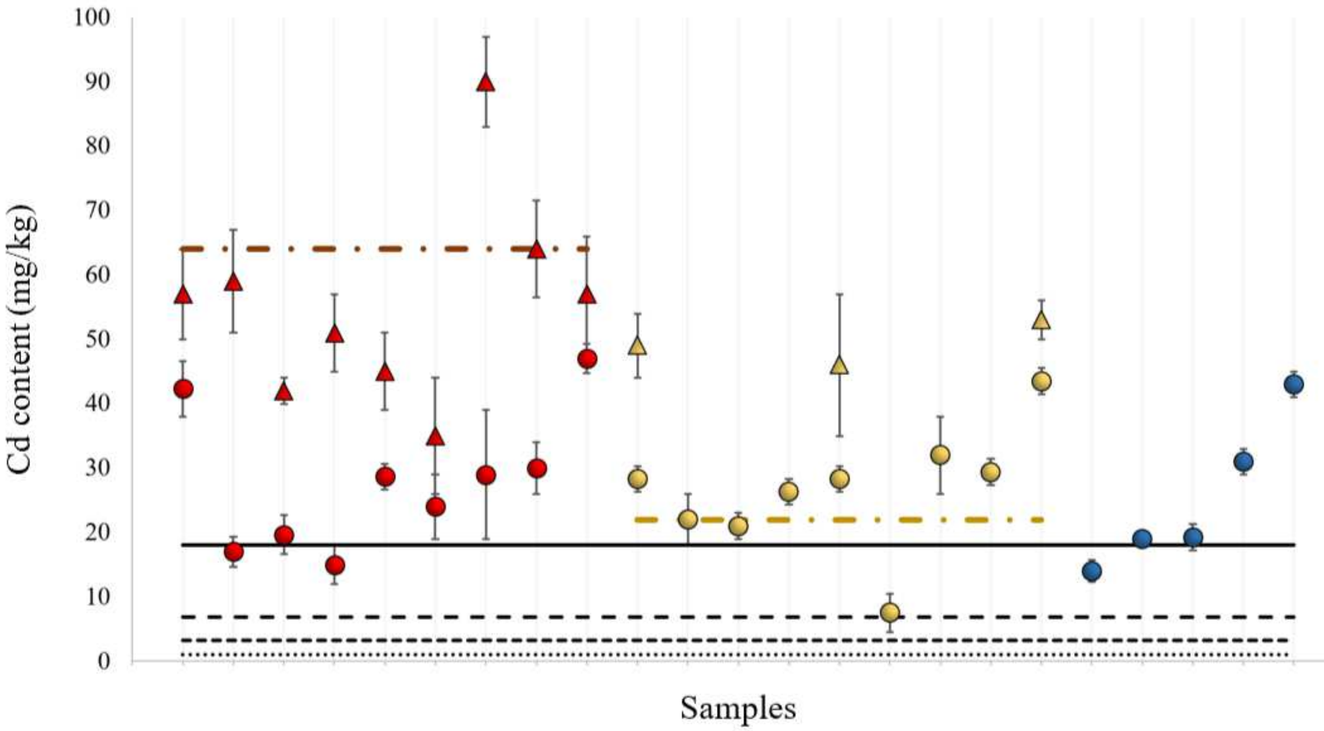

Figure 4. Cadmium concentration in soil (circles) and rock samples (triangles) and concentrations of organic (red line) and chemical (yellow line) fertilizers. Red is for samples from Farm 1, yellow Farm 2 and blue Farm 3. The Cd superior critical threshold (continuous line), highest value in cacao growing soils in Ecuador (dashed line), Cd critical threshold (short dashed lines) and the Cd that is naturally or usually found in most soils (dotted line) are indicated.

3.2. Autochthonous sources of Cadmium

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. Aflizar et al., 2018). 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 (Adriano, 2001; Gramlich et al., 2018). A strong correlation between parental material and Cd content in soils has been previously reported (Smolders & Mertens, 2013; He et al., 2015).

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 the presence of calcareous concretions is significant (Fig. 2; Moreno & Sarmiento, 2002). This was confirmed by our petrographic analyses, which indicates the presence of limestone, marl and shale in all our samples. All rocks analyzed are carbonaceous, thus they can hold substantial quantities of Cd by adhesion and absorption into pores (Fig. 4; Shirvani et al., 2006; Smolders & Mertens, 2013; He et al., 2015; Liu et al. 2017).

Calcite will bind Cd through cation exchanges due to the similar sizes and charges of Ca and Cd (Topcu & Bulat, 2010; Chavez et al., 2015, 2016). This is confirmed by the significant Pearson correlation between Cd and Ca ($p=0.642$, $p<0.05$), which indicates that calcium-rich rocks are the source of Cd, as has been seen in other studies (Argüello, 2015; Chavez et al., 2016; Xia et al., 2020). Carbonate rocks with high Cd content, though the pedogenesis process, tend to produce soils enriched in the metal (Xia et al., 2020).

According to the petrographic analysis, the humic cambisols studied are mainly composed of unconsolidated carbonates and are rich in humus. 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, in agreement with soil forming from the underlying carbonate rocks. While 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. This lack of correlation may be explained by soil and rock heterogeneity and/or difference in number of soil compared to rock samples.

Even though the carbonate rocks can have high Cd concentrations due to their porous structure, it is strongly bound, which makes it less available for plant absorption. In fact, Ca addition has been used as a remediation strategy for high Cd concentrations (e.g. Shirvani et al., 2006; Topcu & Bulat, 2010).

3.3. Allochthonous origin of Cadmium

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 (Moreno & Sarmiento, 2002;Smolders

& Mertens, 2013; de Walque et al., 2018). Even though the region is known for having mining, there is no reported activity near the sampling area, which means this is not a significant source of Cd for our soils. As we established that soils in the area are formed from 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 (Marini et al., 2020). 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 in some cases (Marini et al., 2020). Approximately 85% of phosphate used in inorganic fertilizers is sourced from sedimentary deposits with high Cd levels (Smolders & Mertens, 2013; Robertsa, 2014).

To gauge the relative importance of this Cd source we compared a site with organic fertilizer (Farm 1), to one with inorganic fertilizer (Farm 2) as well as a cocoa farm where no fertilizer is added (Farm 3). Soils with no fertilization show an average of 25 mg/kg of Cd, which we assume to be the base level due solely to weathering of the parental rock. Only a small increase is seen in average Cd concentrations in soils with inorganic fertilizer addition, but soils where the organic fertilizer was used presents average concentrations of 29 mg/kg. Therefore the organic fertilizer seems to 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 (Marini et al., 2020).

In Farm 2, the inorganic fertilizer was used one year prior, but no addition was done close to the time of sampling. This may mean that part of the Cd added with the fertilizer may already have been removed from the soil, and that is why the average metal concentrations are the same as in the case of soils without fertilizer addition. 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 (Fig. 4). Despite Cd content in the inorganic fertilizer not exceeding 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 (Fig. 5; Marini et al., 2020). Besides, there is no certainty 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 (Marini et al., 2020).

The organic fertilizer contained 64 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 European (40 mg/kg; Fig. 4; PPRC, 2010). It is known that Cd bioaccumulates and persist but does not biodegrade thus magnification thought the food chain will take place (e.g. Kabata-Pendias and Szteke, 2015; Mortensen et al., 2018). The organic fertilizer was sourced from chickens and pigs which were fed food residues and organic matter from crops grown in the same soils. It is clear that this resulted in biomagnification of bioavailable Cd that accumulated resulting in extremely high levels of the metal in the organic fertilizer (Fig. 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. Although the addition of fertilizer may further enrich the metal in soils, we found no significant correlation between soil and fertilizer Cd conecntrations, indicating that this is not the main factor controlling total Cd in soils.

The metal can also be reintroduced into the soil through the falling of the plant's leaves or branches, and in some cases, farmers will leave plant debris as a fertilizer (Chavez 2016; Argüello et al., 2019). 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 20 cm sampled) may in part be due to the accumulation over the years of the metal from leaves and husks. In farms in Ecuador 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 (Barraza et al., 2017). The use of vegetation waste originating within the same plantation as fertilizer will recirculate bioavailable heavy metals, though the relative importance of this recycling process as a contributor to Cd accumulation in cacao beans is yet not 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 cultures.

3.4. Soil factors affecting Cadmium bioavailability

Soil Cd content is directly correlated with the bioavailability and cycling of the element in soils. Not all the Cd present in soil 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 (Mortensen et al., 2018). Besides the actual content of Cd in soils, several soil properties affect the Cd bioavailability and consequent root uptake (Mortensen et al., 2018). High electrical conductivity and salinity concentrations as well as loamy and clayey soil textures result in higher Cd availability; luckily 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 (Gramlich et al., 2018; Mortensen et al., 2018).

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. Kabata-Pendias, 2010). However, we do not observe Cd leaching, which could be explained by the high slope of the cacao plantations we examined, causing 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 biding (Gramlich et al., 2018; Mortensen et al., 2018).

The pH values of our soils ranged between 5.5 and 7.8, with little variation between farms and within the ideal range for retention of Cd within the soil matrix (Mortensen et al., 2018). At pH higher than 5.5 the metal converts into insoluble carbonate and phosphate forms, making it unavailable (Kabata-Pendias 2010). Even when the soil pH is in the ideal range, like in ours samples, Cd remobilization absorption and accumulation in plant tissues may still occur: 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. Dong et al., 2007). 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 (Remigio, 2014; Argüello et al., 2019; Zug et al., 2019). While microheterogeneity may partly explain Cd absorption, the high concentrations in beans could also be linked to the extremely high levels of Cd in soils.

The manganese and potassium content of soil have a minor negative influence on plant Cd incorporation, probably due to ion competition (Gramlich et al., 2018; Argüello et al., 2019). Studies have shown that when Mn is present on a ratio above 20 to 1, Cd uptake appears to be reduced (Gramlich et al., 2018; Argüello et al., 2019). We find a ratio of 47.5 Mn to 1 Cd, which would undoubtedly result in a smaller Cd uptake by the plants in the area. 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 (Kabata-Pendias & Szteke, 2015). Teherfore, soil organic matter will efficiently bind Cd^{+2}, especially if associated with pH levels between 5.5 and 7.5 (Mortensen et al., 2018). 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} (Remigio, 2014; Mortensen et al., 2018). The sampled soils had from 1.7 to 7 grams and thus could potentially reduce metal availability. The elevated organic matter coupled with the neutral to basic pH has been previously used to explain the lower than expected Cd levels in seeds in the area (de Walque et al., 2018). Since factors such as the pH, organic matter content and presence of carbonates mitigate the plant's uptake of the metal as they buffer and absorb the metal, we conclude that the Cd availability is considerably below what it potentially could be, given the metal concentrations found in our soils. Without these mitigating soil characteristics, the exposure and availability of the metal would likely pose a much higher health risk (He et al., 2015) and could mean even higher accumulation in cacao beans (Mortensen et al., 2018). This would ultimately make them toxic and not suitable for consumption or commercialization. In fact, using the reported ratio of accumulation of 1:4 in beans, and based on the highest Cd content reported for beans of 9.34 mg/kg, this would mean that only a maximum of 2,3 mg/kg of metal will be bioavailable for plant uptake (Brus et al., 2002; Chavez et al., 2015; Khan et al., 2017; de Walque et al., 2018). 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 (Meter et al., 2019; Rodríguez Albarracín et al., 2019).

3.5. 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 taken by considering actions from farm to final product that are adapted to the specific conditions of the cacao value chain in question (Bravo et al., 2018; de Walque et al., 2018; Zug et al., 2019).

Reducing the addition of organic fertilizers to minimize the amount of bioavailable Cd accumulation might be an easy and effective strategy (Marini et al., 2020). But of course a better approach would be to test the fertilizers of both chemical and organic nature to guarantee that they have low metal values and can be applied as needed.

While the addition of soil amendments that alter pH 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 (e.g. Liu & Hue, 2001; Chavez et al., 2016). Amendments would not have an impact in the present study area since the parameters are already optimal.

Another potential solution is leaching, which can remove fertilizer and contaminant components over time (Argüello et al., 2019). 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) (Dermont et al., 2008; Torres et al., 2012), 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 Cd.

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 (Engbersen et al., 2019). However, this strategy can be 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 (Sposito, 1983; Bravo et al., 2018; de Walque et al., 2018).

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 (Chavez et al., 2016; Bravo et al., 2018).

4. Conclusions

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

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 significantly diminish Cd bioavailability, there is a high metal content in cocoa beans of the area.

We consider phytoremediation and biological amendments to be relatively fast and cost-effective solutions to the observed Cd enrichment.

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