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Cadmium Accumulation in Theobroma cacao L. soils Adjacent to Banana Plantations, in the Buena Fe canton, Los Ríos Province

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Abstract
The present investigation was carried out with the purpose of determining the accumulation of cadmium in soil of Theobroma cacao L. under the influence of banana plantations located in the Buena Fe canton, Province of Los Ríos Ecuador. Soil samples were taken at two depths 0 -20 cm and 20-40 cm, and Ca content was determined, To analyze the data, a multivariate analysis and multiple linear regression were applied and to measure the effect between variables, a complete randomized design was applied, the Tuckey Test was used (P=0.05); Finally, a comparison was made using the non-parametric Kruskal Wallis statistical test, with the help of the INFOSTAT software. It was determined that the average Cd was 2.24±1.5mg.kg1 for the depth 0-20 cm and 20-40 cm respectively and with an average of 1.88 Cd mg/kg, exceeding the maximum permissible limits. The high cadmium contents in the first layer of soil and slight decrease with depth allow us to conclude that the presence of cadmium is possibly of anthropogenic origin, so it is necessary to look for viable mitigation alternatives to reduce Cd content in soils with cocoa cultivars under the influence. of banana plantations.

Keywords: *Pollution, heavy metals, agricultural practices, physicochemical properties.*

I. INTRODUCTION

Cocoa (Theobroma Cacao l.) It is one of the main fruits consumed worldwide, due to its presentation in chocolate. Its consumption rate around the world was 3.6 million tons for 2010 and in the last period (2018-2019) the production range was almost 5 million metric tons (Mt). It has been estimated that cocoa production involves between 5 to 6 million farmers globally, .(Del Prete & Samoggia, 2020)(García-Briones, Pico-Pico, & Jaimez, 2021)(Carr & Lockwood, 2021)

In the period 2019-2020, world cocoa production was 4.7 million tons, of this annual production, 18.4% (0.9 million Mt) were produced in Latin America, Ivory Coast and Ghana are the first two countries with the highest production (2.1 and 0.8 million Mt, respectively) and Ecuador the third (0.32 million Mt). In January 2020 the price per ton was 2603 USD. The lowest prices were recorded in the month of July 2020, paying 2100

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USD/Mt, then the increase began to reach 2407 US Mt, at the end of December of the same year.(García-Briones, Pico-Pico, & Jaimez, 2021)(ICCO, 2021)(García-Briones, Pico-Pico, & Jaimez, 2021)

The Province of Los Ríos has a harvested area of 96200, with a production of 41,187 Tm and a yield of 0.4 (Tm/ha) which occupies the second place as a cocoa producing province, more than 60,000 people are directly involved in the activity. Therefore, the cocoa chain participates with 4% of the National Economically Active Population (EAP) and 12.5% of the Agricultural EAP, at the national level there are 180,336.00 hectares planted and in the Province of Los Ríos it is 61,937.00ha(CFN, 2018)(Carranza Quimí, Angulo Castro, Cedeño Risco, & Prado Cabezas, 2020)$^{-1}$ and its output is 2822,585.00Tm.

The maintenance of these plantations is due to the combination of several fertilizers and pesticides and their excess is causing severe environmental damage to the soil, water and air; Agronomic practices favor the accumulation of Cd in soils, as well as river water for irrigation, which is enriched with Cd due to agricultural activities, burning, phosphorus fertilizers, natural sources, and air pollution.

Another important aspect within Cd studies in Ecuador is the lack of focus of the analyses with respect to the season of the year (winter or summer), since the bioavailability of the metal is affected by the water balance within the soil and the pH , , , a (S., Thornton, Farago, & Ashmore, 2015) (1998)(Cheng, y otros, 2014)In addition, intensive banana cultivation uses a wide variety of agrochemicals (pesticides and fertilizers) that are dispersed through aerial fumigation over large areas of crops. According to , Cd pollutant particles are dispersed through the air until they settle within the abiotic resources. Many of the phosphate fertilizers contain Cd in their chemical composition and banana crops are implemented to improve their yield and contribute to the increased absorption of water and nutrients that are essential in the development of the fruit (Cheng, y otros, 2014)(Imseng, y otros, 2018)(Bolfarini et al. 2020); .(Imseng, y otros, 2018)

Given the need to glimpse the reality in which the soils are found, this research sought to determine the accumulation of cadmium in the soil of Theobroma cacao L. under the influence of banana plantations located in the canton of Buena Fe, Province of Los Ríos, Ecuador.

II. MATERIALS AND METHODS

The present research was carried out in cocoa farms adjacent to banana plantations in the Buena Fe Canton (Figure 1), bordered to the north by the province of Santo Domingo de los Tsáchilas, to the east by the canton of Valencia, to the south by the province of Guayas and the Canton of Quevedo and to the west by the province of Manabí. The geographical coordinates are 0° 53′ 55" South, 79° 29′ 20" West, LatitudeN -0.898572, and Longitude E -79.4889 (DB-City, 2021)the Temperature is 22.6 C, Average Relative Humidity 90,1%; Heliophany, annual, daylight hour 755.2 and Precipitation/year 6100 mm (INAMHI (2023).

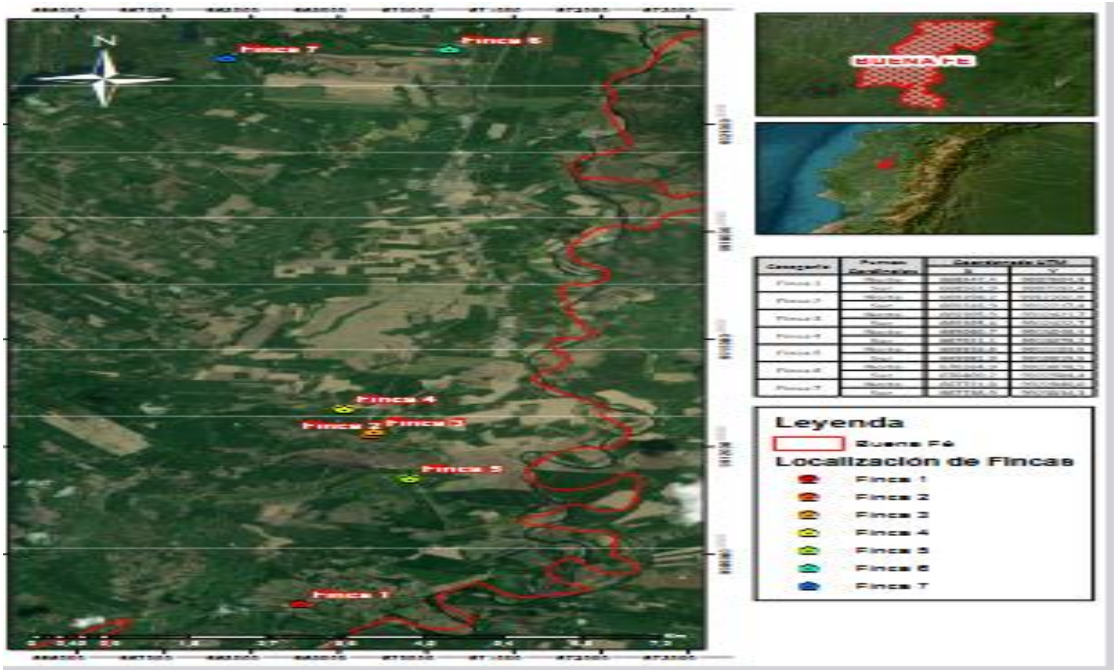

Figure 1. Geographic Location of Study Area, 2023

A bifactorial design of 7 x 2 with a DCA was applied. Soil samples were taken in a zig-zag pattern, in 7 sampling farms and at two depths (0 - 20 cm and 20-40 cm) for the highest amounts of physiologically active roots and the highest concentrations of Cd following the methodology of; ; . The concentration of cadmium as a heavy metal present in the soil was considered as a dependent variable (soil quality) and as an independent variable.(Chavez E. , y otros, 2015)(Gramlich, y otros, 2018)(Jaramillo, Medina, Recalde, Pastás, & Bedoya, 2015)

ISO/INEN 2859 sampling and soil characterization according to the World Reference Base for Soil Resources were considered; , the (FAO, 2015) (Imseng, y otros, 2018)(Jaramillo, Medina, Recalde, Pastás, & Bedoya, 2015)Field Capacity (cc) based on texture, while the finer the texture, the higher the percentages of water in the soil, both at the DC and at the point of wilting. A good soil structure also increases the fraction of useful water. The water content by weight (HP%) to Field Capacity is the weight of water divided by the weight of dry soil, the following equation was applied:(García & Dorronsoro, 2015)

$$\text{HP\% CC} = \frac{(\text{Peso Fresco a CC} - \text{Peso suelo seco})}{\text{Peso suelo seco}} * 100$$

Soil density

It corresponds to the weight of the unit volume of the soil solids, which was obtained from the dry weight of the soil sample and the volume occupied by the solids in the sample. The volume was evaluated by means of an apparatus called a pycnometer, and the procedure corresponds to the application of Archimedes' principle, that is, it determines what volume of liquid the solids displace when they are submerged. Based on the following equation:(Rubio Gutierrez, 2010)

$$\text{D.r (g cm} - 3 \text{ o} \frac{\text{Mg}}{\text{m}} - 3 = \frac{\text{Peso de los sólidos de la muestra o peso seco}}{\text{Volumen de los sólidos de la muestra}}$$

Soil pH

The pH of the soil allowed us to know the degree of acidity or alkalinity present in the soil, a fundamental value in agricultural production, it allows us to detect if there are imbalances of elements or other nutritional problems, it was considered:

- Soil sample, previously dried at 40ºC for several hours.
- Sieving the sample by 2 mm.
- Sample of 20 g of soil.
- Add the sample to a beaker with 50 ml of distilled water.
- Shake the mixture for 2 minutes.
- Let the mixture sit for 15 minutes.

The pH was measured in the supernatant, i.e. in the liquid above. To do this, electric pH strips or meters were used based on the . Chemical analyses were performed at the San Marcos Accredited Laboratory.(Calle Shagñay, 2021)

Cadmium in cocoa soils.

Measurements of Cd concentrations in soils were made using analytical methods. Both the extraction protocol, the choice of the analytical instrument, and its calibration, play an important role in the determination of Cd. (Meter, Atkinson, & Laliberte, 2019)

For the analysis of the data, descriptive statistics (ADEVA) was applied, a Pearson correlation analysis, in order to reveal the correlation of cadmium in soil between farms, an analysis of variance was also performed to establish the statistical differences between the treatments and repetitions used and these results were compared with the national regulation that indicates that for cadmium the standard is 0.5 mg/kg).(Ministerio del Ambiente, 2015)

(MAE, 2015) and to determine whether there are statistically significant differences ($p<0.05$) in cadmium concentrations in soils from the canton of Buena Fe, a comparison was made using the non-parametric statistical test of Kruskal Wallis, with the help of the INFOSTAT software, the components p, k, Nh4, Mg, S, Cu, Fe, Mn, Zn, Cd, texture, organic matter, was analyzed by principal component analysis to establish the relationship between the farms and soil quality.

III. RESULTS

Cadmium Dynamics in Soil

Cadmium is one of the metals that has gained importance in recent decades due to its harmful effects on human health, as it can cause chronic diseases, and this is evidenced by the growing number of affected populations, according to the WHO, these figures amount to more than 50% of the world total. In rural areas, the presence of cadmium in the atmosphere is estimated to average 0.1 to 5 ng/m3, while urban areas have a higher level of 2 to 15 ng/m3 and industrialized areas 15 to 150 ng/m3. Multiple studies mention that atmospheric gases represent the first cause of Cd in the environment, due to the burning of fossil fuels, mining and metallurgy processes. Also, the burning of biomass as well as the incineration of municipal solid waste (this means that the particles disperse and travel long distances until they settle in the soils or aqueous environments of nature. (Valencia López & González Osorio, 2022)(Cheng, y otros, 2014)(Imseng, y otros, 2018)

Cadmium in soil comes from the application of phosphate fertilizers to the soil. In this medium, cadmium is absorbed by plants, due to its similarity to zinc, and thus exerts its toxic action. When it enters the soil, cadmium is quite mobile and is evenly distributed along the soil profile. It can be found at different depths and in different molecular forms, occupying cation exchange sites in the clay fraction (lamellar silicates, oxides and hydroxides of Fe and Mn, etc.) and humic fraction; Adsorbed or co-precipitated together with oxides and hydroxides, precipitated as carbonate in soils at pH greater than 7; precipitated as sulphur in reducing soils, and adsorbed specifically to humic material forming essential chelates, etc. In contaminated soils the predominant soluble cadmium species are the free ion Cd2+ along with other neutral species such as CdSO4 or CdCl2, present in increasing amounts where the pH is greater than 6.5. Cadmium has no essential biological function and both it and its compounds are highly toxic to plants and animals.(González Osorio & Pazmiño Rodríguez, 2020)(Del Prete & Samoggia, 2020)

When analyzing the pH results, the average values amount to 9.96 (table 1), a value that is within the national environmental standard range (6 – 8), which allows us to indicate that they are alkaline soils, the result of cadmium in the soil registers values above the maximum permissible limit (0.5mg/kg), at a depth of 0-20 cm it is 2.24 Cd mg/kg and 20-40 is 1.51 Cd mg/kg, values that when being compared to the standard value established in Ministerial Agreement 097, Annex II, in the two soil layers studied, the Cd mg/kg is higher, therefore the soils are contaminated, values that coincide with what was reported by the soils of Ecuador covered by crops, which is due to the fact that it is the result of the age of the crops in combination with organic and conventional practices ($P \leq 0.0$) of Cd, however, must be considered in the variable "age" and organic management practices totally change its content.(SEMARNAT, 2021)(Argüello, y otros, 2019)

The study carried out in the Provinces of El Oro and Guayas estimated that the probable source of contamination of cd in soils is due to the use of river water for irrigation, which is enriched with Cd due to artisanal mining activities linked to gold extraction. Another study of cadmium in the soil of cocoa crops accompanied by management with ecological practices in three farms in the Province of Esmeraldas and Sucumbíos found high levels of cd, despite the fact that agrochemicals such as phosphate fertilizers are not used, despite this, the enrichment of Cd in these sites is due to natural sources and atmospheric pollution; On the other hand, . He states that the addition of Cd to the crop comes from the decomposition of the cocoa tree's own residues (leaves and branches) that are used as natural fertilizers in the crop. (Chavez E., et al., 2015) (Barraza, y otros, 2022) (Imseng, y otros, 2018)(Barraza, y otros, 2022)

It is important to emphasize that bioavailability is associated in the way of predicting soil solution at cd concentrations where Cd leaching occurs by infiltration of water into lower soil layers and is determined by Cd concentration and the amount of water (precipitation, evapotranspiration and change of water content in the soil). Bioavailability depends fundamentally on pH as it is the main factor governing metal solubility and availability for plants, i.e., metal solubility tends to increase at low pH levels and decrease at high pH values, therefore, a neutral pH tends to be an immobilization mechanism. (Rieuwerts, Thornton, Farago, & Ashmore, 1998)(Imseng, y otros, 2018)(Rieuwerts, Thornton, Farago, & Ashmore, 1998)

The soil properties that must be considered in parallel for the bioavailability of Cd are: cation exchange capacity (CEC), organic matter content, the percentage of organic carbon in the soil and electrical conductivity (EC). In the case of the (Argüello, et al., 2019)(Imseng, y otros, 2018)(Rieuwerts, Thornton, Farago, & Ashmore, 1998)Latin America and the Caribbean (LAC), in cocoa-producing sites and regions, are also battling Cd contamination in their crops. Currently, Cd is not only a problem in LAC, but in countries such as Ecuador, Colombia, Peru, in the latter a study was carried out in the Province of Bagua located in the Amazon in native cocoa tree crops that grow under ecological practices, weight to this, the concentrations of Cd in the soils varied between 1.02 and 3.54 mg kg, where 62% of the samples exceed the limits established in Peruvian regulations (1.4 mg kg). $^{-1-1}$(Oliva, Rubio, Epquin, Marlo, & Leiva, 2020)

In countries such as Honduras, on the other hand, the cocoa soils of 55 farms were characterized as uncontaminated, however, it is evident that the high concentration of Cd was found in the first centimeters (0-10) with 0.25±0.02 mg kg and 0.16±0.01 mg kg in the 10-15 cm. Both studies in both Peru and Honduras led us to conclude that despite their concentrations of Cd in the soil (within and outside the permissible limits), it was evidenced that almonds and parts of the cocoa tree had high concentrations, which makes us estimate that it is necessary that Cd studies always start with evaluations of Cd in cocoa soils. $^{-1}$ $^{-1}$ (Gramlich, y otros, 2018)

The study mentions that Cd is highest during the dry season in sediments of the Huallaga River (May-August) with values between 1.28 and 2.57 ppm. In China, a study was carried out on heavy metals in banana crops on Hainan Island, where they determined a wide contamination by heavy metals, among them, we have Cd whose concentrations varied from 0.43 to 3.21 mg kg-1, which was 5% higher than in those organic banana crops. The likely response to this contamination is the use of commercial organic fertilizers and compost residues that are predisposed in the plantations, as well, the concentrations of Cd were reduced compared to the other heavy metals, and it is due to the leaching that occurs to deep layers of the soil. (Huamaní-Yupanqui, Huauya-Rojas, Mansilla-Minaya, Florida-Rofner, & Neira-Trujillo, 2012)(Lin, Ouyang, Huang, & Huang, 2010)

The seasons of the year are important in the solubility of Cd, due to the amount of precipitation that changes the pH of the soil. In Ecuador there are several studies that evaluate Cd in concentrations both in the winter and summer periods. Soil samples in Sucumbíos for both Nacional cacao and CCN 51 averaged 0.52 mg kg^{-1} and 1.10 mg kg^{-1} in the surface layer, where the average annual precipitation is >3000 mm. While 0.02 mg kg(Argüello, y otros, 2019)$^{-1}$ at 6.90 mg kg^{-1} were the range of variation of Cd concentrations in soil with National Cocoa and CCN-51 within a large study of 159 cocoa crops nationwide in Ecuador (Argüello et al., 2019).

In Ecuador, provinces of Guayas and El Oro, an investigation was carried out with 19 soil samples with cocoa, it was shown that the Cd was between 0.88 mg kg^{-1} to 2.45 mg kg-1, values that also exceed the permissible limits by the TULMAS, which is mainly due to average annual rainfall of 575.8 mm, which through runoff drags particles from contaminated soils generating high values of cd content. In relation to the area of Sucumbios; . It states that the same trend was evidenced in investigations of Cd content in soils, the results of which showed a relationship between the high content of Cd in soil (average of 1.54 mg kg (Barraza, et al., 2022) (Chavez E. , y otros)$^{-1}$) and its cocoa almonds. Therefore, the rainfall range or season of the year could play a key aspect in the analysis of the Cd, in turn, also, Ecuador has many regions where Cd levels are exceeding the limit set by the United States Environment Agency (EPA) of 0.43 mg kg(Chavez E. , y otros)$^{-1}$ for soils, European regulations establish a maximum of 3ppm in agricultural soils; and so also the soil quality criteria in Ecuador of 0.5 mg kg(Huamaní-Yupanqui, Huauya-Rojas, Mansilla-Minaya, Florida-Rofner, & Neira-Trujillo, 2012)$^{-1}$ for Cd (Environmental Quality Standard for Soil Resources and Remediation Criteria for Contaminated Soils - Annex II, 2015).

Another study carried out found that in Ecuador there are several sites with high Cd content in cocoa crops, in its cadmium dispersion map it showed that cocoa almonds with Cd content are identified as the areas most contaminated with Cd in soils, which are located in the provinces of Esmeraldas, Manabí, Orellana and El Oro, where their concentrations are 0.91 to 10 mg kg(Argüello, y otros, 2019)$^{-1}$. In the Province of Los Ríos the ranges range from 0.33 to 0.60 mg kg^{-1} Only one focal point with a high concentration of 1.31 to 10 mg kg is identified^{-1} between the cantons of Quinsaloma and Ventanas (Argüello et al., 2019), which can be added to the factor of banana plantations grown in the canton of Ventanas. In this region there is only a single evaluation on 12 farms in Quevedo, Mocache, Quinsaloma and Valencia, whose research is aimed at Cd in cocoa almonds and soil, whose results showed that Quevedo has a high concentration in soil (0.35 mg kg^{-1}) compared to the other cantons 0.22 mg kg^{-1}, 0.16 mg kg^{-1} and 0.20 mg kg^{-1}, respectively). In addition, soil concentrations are associated with high almond concentrations of 1.67 mg kg(Baraja Palomo, 2019)$^{-1}$ in Quevedo . The same trend was found in the soils of the Buena Fe canton, where the sampled sites can be categorized as contaminated soils because they are above the permissible limits (Table 1).(Baraja Palomo, 2019)

Table 1 Cadmium concentrations in cocoa soil at depths of 0-20cm in farms adjacent to bananas in the Buena Fe canton of Los Ríos province, Ecuador

Depth	PH	Standard Value	Cd mg/kg	TULSMA Standard Value
0 – 20 cm	7,06	6 – 8	2,24	0,50
20 – 40 cm	6,86	6 – 8	1,51	0,50
average	6.96	6-8	1.88	0.50

Elaboration: Authors

Source: Accredited Laboratory "Grupo Químico Marcos"

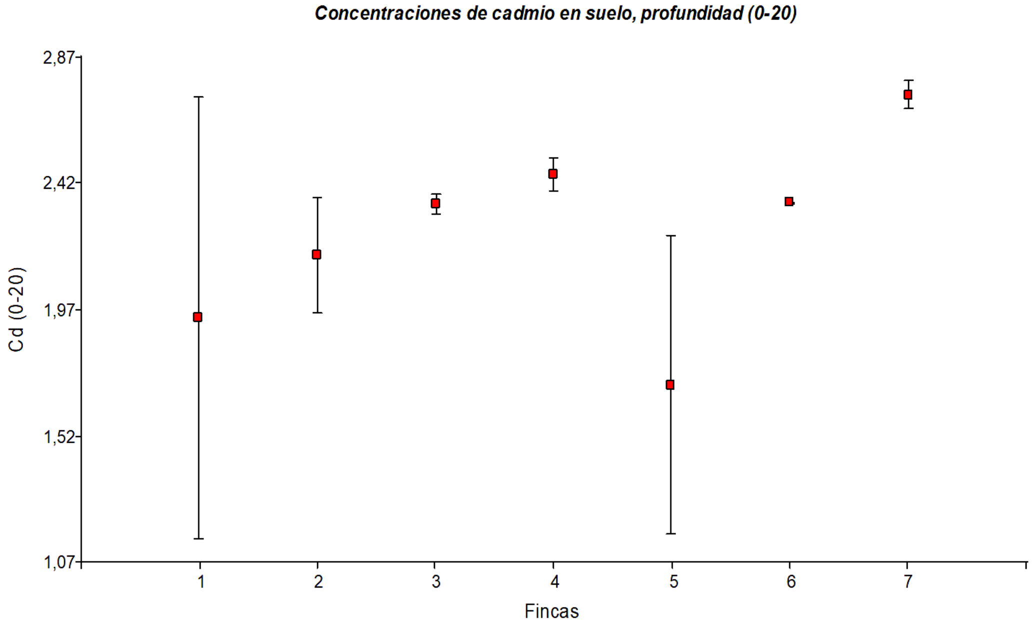

Figure 2. Cadmium concentrations in cocoa soil at depths of 0-20cm in farms bordering bananas in the canton of Buena Fé in the province of Los Ríos, Ecuador

According to the Kruskal Wallis test, it was shown that there are no significant differences (H=7.43; p=0.2830) in cadmium concentrations in the soils of the Buena Fe canton from seven farms at a depth of 0-20cm (Figure 2). The same trend is shown at the depth of 20-40cm for cadmium concentrations (Figure 3).

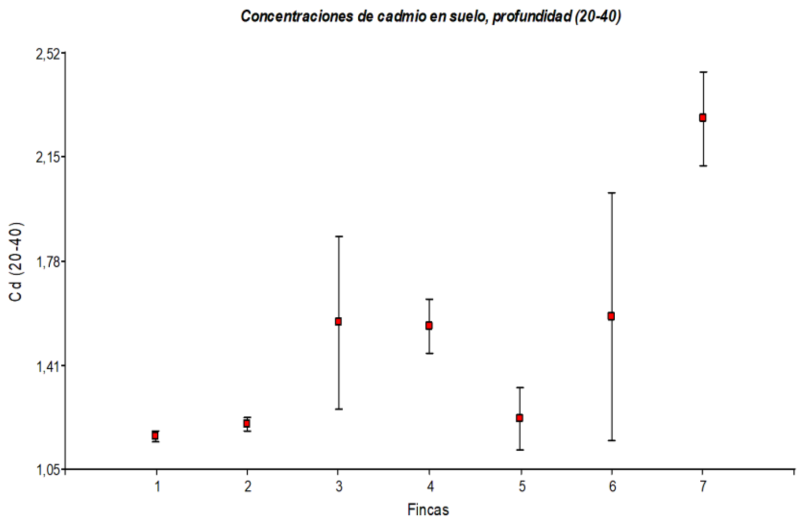

Figure 3. Average concentrations of cadmium in cocoa soil at depths of 20-40cm in farms adjacent to bananas in the canton of Buena Fe, province of Los Ríos, Ecuador

Table 2. Kruskal Wallis test on cadmium concentration at depth of 0-20-40 cm and 20-40 cm in cocoa soils on farms bordering bananas in the canton of Buena Fé, province of Los Ríos, Ecuador

CD	Half	D.E.	Median	H	p
(0-20)	2,08	0.64	2.35	0.92	0.3829
(0-20)	7	2.41	0.28	2.38	
(20-40)	1,43	0,49	1,23	1,47	0.2325
(20-40)	1.59	0.40	1.45		

Based on the Kruskal Wallis test, it was shown that there are no significant differences (H=0.92; 2.38; p=0.3829) in cadmium concentrations in the soils of the Buena Fe canton at a depth of 0-20cm, the same trend is observed in the depth of 20-40cm, whose p values are 0.2325 and H=1.47 (Table 2). A concentration of 0.08 mg/kg of cadmium is found in the clay loam soils but they are not the same as those reported by the person who determined values of 0.11 mg/kg, when analyzing all these results we can say that in the farms different values of cadmium were found and exceed the permissible values of Tulsma which is 0.5 mg/kg-1 and . (Britannica, 2023) (Mar & Okazaki, 2012)(Huamaní-Yupanqui, Huauya-Rojas, Mansilla-Minaya, Florida-Rofner, & Neira-Trujillo, 2012)(De Los Ríos silva, 2021)(Ministerio del Ambiente, 2015)(Ministerio del Ambiente, 2015)(Calle Shagñay, 2021)

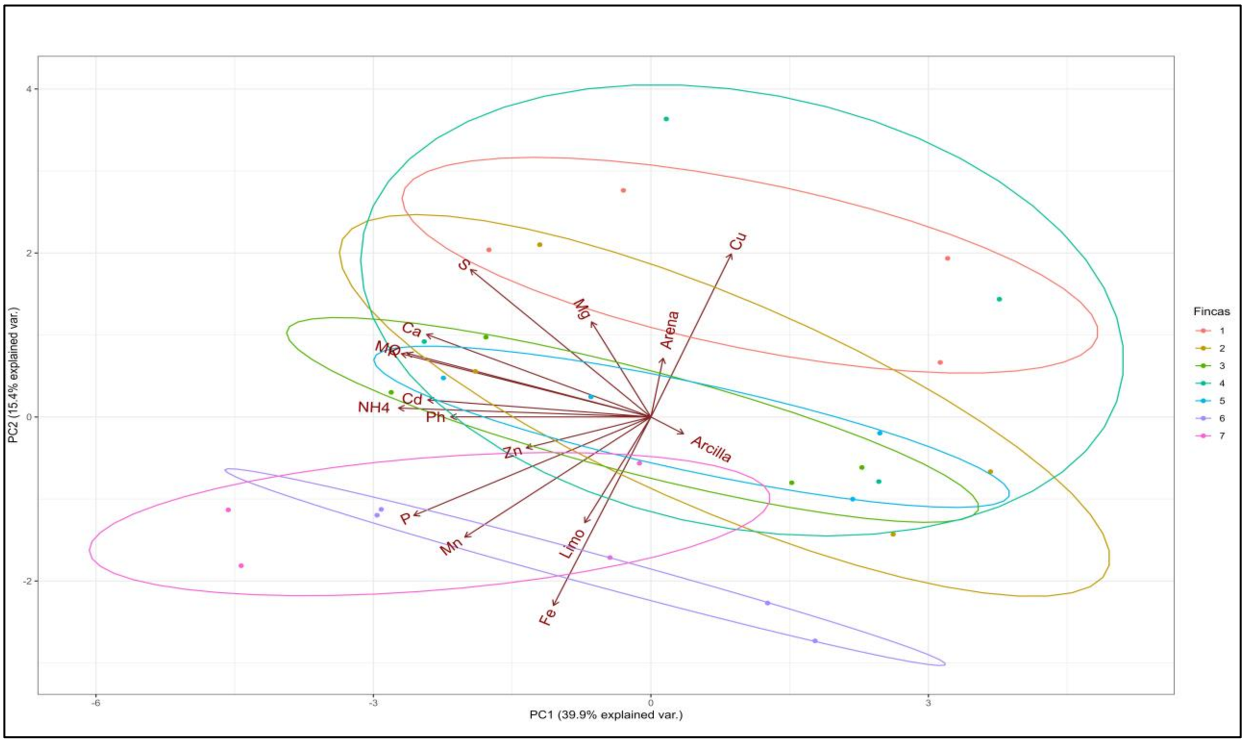

Figure 4. Principal component analysis (biplot) of the content of p, k, Nh4, Mg, S,Cu, Fe, Mn, Zn, Cd, texture, organic matter in the soil of cocoa plantations

Figure 4 shows the analysis of principal components of the elements p, k, Nh4, Mg, S, Cu, Fe, Mn, Zn, Cd, texture, organic matter, and in Table 3, the range of significance is recorded, values that coincide with those reported by cadmium concentrations from 0.34 to 2.83 mg.kg(Zhao, Tang, Song, Huang, & Wang, 2022)$^{-1}$for Lead from 42 to 88mg.kg−1 and high values for p, Fe, Zn, Mg, which demonstrates the serious global crisis that crops are currently facing due to the presence of toxic metals in soils and food that directly affects the sovereignty and food security of countries worldwide.

IV. CONCLUSIONS

According to the study of the soil analysis carried out at different depths in farms dedicated to the production of cocoa, it was found that the concentrations of cadmium did not present statistical difference between them and are above the limits permissible by the TULSMA, which shows that the soils are contaminated by cadmium in concentrations of 2.24 and 1.55 Cd mg/kg.

The non-parametric statistical test of Kruskal Wallis showed that there is contamination due to the presence of cadmium, which demonstrates the serious global crisis that cocoa is currently facing due to the presence of the metal in the soils that directly affects food security and sovereignty in the province. and the countries they present.

GRATITUDE

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