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ORIGINAL PAPER

Cadmium distribution in soils, soil litter and cacao beans: a case study from Colombia

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Abstract

Cadmium is a toxic non-essential metal for almost all living systems. It is one of the biggest challenges for farmlands and the food chain because of its toxic effect on human health. This research aims to determine the Cd content in soils, litter and cacao beans, following the Cd fluxes within each cacao system using the two-dimensional electrical resistivity tomography technique. The study was carried out in four farms located in the Magdalena basin in Antioquia, Colombia. The farms showed a heterogeneity in relation to cacao cultivars, altitude, topography and geology. The soil cation electrical capacity, pH and soil organic matter levels, as well as the Al, $Al^{3+}H^{+}$, Ca, K, Mg and P contents were measured at different depths. Moreover, the Cd content was correlated to the resistivity values of samples taken in situ using ERT. Soil $Al^{3+}H^{+}$ and the altitude of the farms fitted as the best predictors of the beans' Cd content. Furthermore, the Cd content in soils from the assessed farms ranged between 1.22 and 2.03 mg kg^{-1}. The Cd content in cocoa beans ranged from 0.07 to 1.44 mg kg^{-1}, with a value of 0.40 mg kg^{-1} on average. The resistivity values obtained in field showed a high correlation with the soil Cd content determined ($R^2 = 0.82$). The predictive tomography plots highlighted topsoil Cd dynamics between litter, amendments and fertilizers. Therefore, these results underlie the utility of the combined geophysical techniques and soil chemical properties including the analysis of fertilizer amendments to improve the understanding of Cd dynamic.

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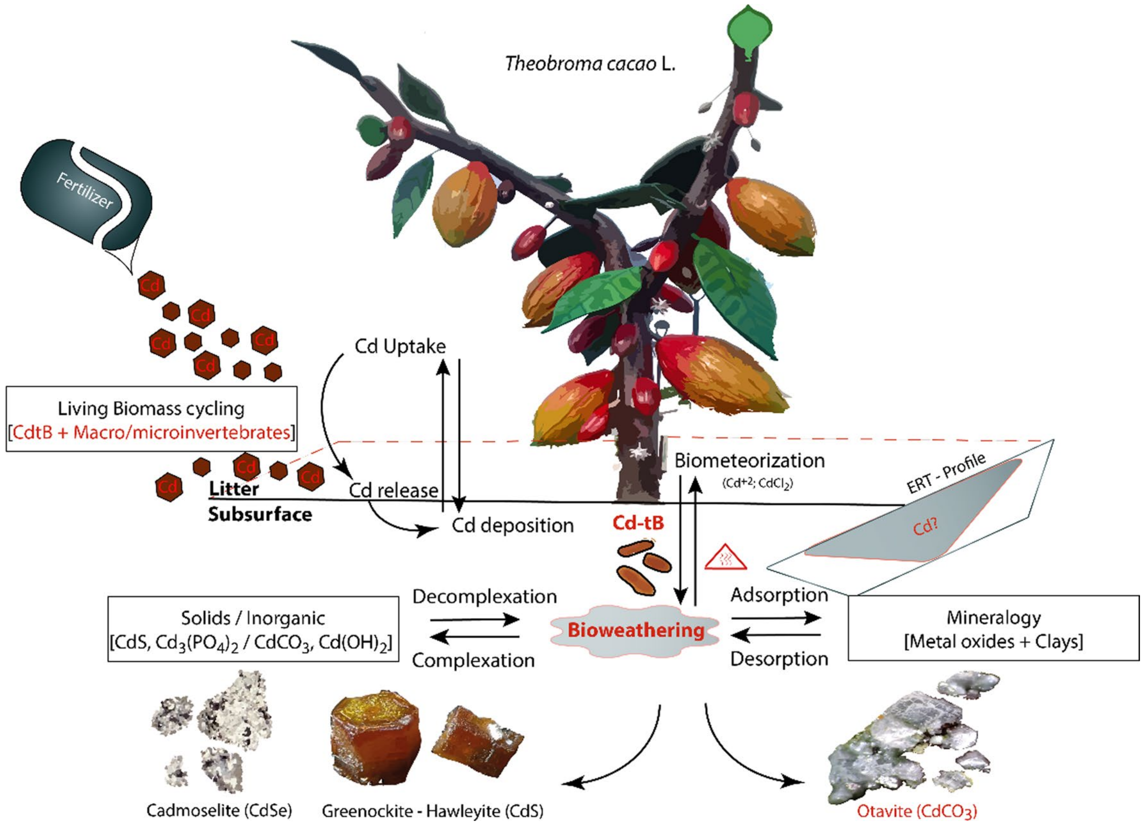
Graphic abstract



Keywords Cadmium · Cacao soils · Cacao beans · Soil parameters · Electrical resistivity tomography · Fertilizers

Introduction

Cadmium (Cd) is a non-nutritive element and has adverse effects on living systems (McGrath 1999). Therefore, no beneficial effects have been observed on biological systems related to metal consumption. Cd can be found in eight fractions (Christensen and Haung 1999), where the free Cd^{2+} fraction in soil solution is absorbed at a faster rate (Helmke 1999). The labile fraction of Cd in soils might also be found as phytoavailable, which means that the Cd flux pumping through the ion exchange cellular system in vascular tissues of hyperaccumulator plants is higher (Menzies et al. 2007). Moreover, Cd solubility in soils is affected by several chemical properties, where pH and soil organic matter (SOM) are the critical physical properties influencing the dynamics of inorganic complexes and metallic oxides, which influence the Cd total content in soils (Yi et al. 2020).

In cacao-growing soils, the presence of Cd in both surface and subsoils is one of the biggest challenges in Central and South American cacao-producing countries, such as Honduras, Colombia, Ecuador and Peru (Arévalo-Gardini et al. 2017; Bravo et al. 2018; Gramlich et al. 2018; Argüello et al. 2019), due to the mobility and the high loading ratio of this metal which moves forward from the soils into the cacao beans.

Particularly in Colombia, in some cacao-growing regions, higher Cd contents have been found in both soils and beans, especially in farms located in the northeast (Bravo et al. 2018). This is an issue, since the current *Codex Alimentarius* regulation has established the maximum permissible levels of Cd in chocolate and end-products derived from cacao beans (Points 2017).

Interestingly, Colombia has several cacao-growing regions with diverse agroecological features, including climate conditions, soil types and crop systems. This has resulted in the production of fine flavour cacao beans, mainly derived from the 'Criollo' and 'Trinitario' cacao varieties across the country (Barrientos et al. 2019). The Antioquia district, after Santander, is the second largest producing region of cacao where important productive areas are located in the basin of the Magdalena valley, limiting with the Santander district. This region shows a topography marked by complex mountain systems as part of the central cordillera, with slopes ranging 25–50%, loams to sandy-loam soil textures, with moderate outcroppings ≤ 50% (Malagon and Pulido 1995), annual mean temperature of 27.1 °C and 2270 mm of annual precipitation on average (Poveda 2006).

The district of Antioquia is located in the northwest region of Colombia. The geological depositions and mountain complex systems are characterized by great geodiversity (Rivera et al. 2013). The rock outcroppings in this area vary in age from the Proterozoic–lower Paleozoic to the Holocene, and in origin, from igneous to metamorphic and sedimentary (González et al. 2001). Cadmium concentrations are generally higher in sedimentary rocks than in igneous rocks (Alloway and Steinnes 1999), with concentrations ranging from 0.07 to 0.25 mg kg^{-1} Cd in igneous rocks, from 0.11 to 1.00 mg kg^{-1} Cd in metamorphic rocks and from 0.01 to 2.60 mg kg^{-1} Cd in sedimentary rocks (Traina 1999).

From mostly affecting Cd dynamics in cacao-growing farmlands and cacao beans, it has been observed that several soil parameters should be assessed. Particularly, one could take into account: 1. soil pH, as highlighted in previous studies (He et al. 2015), showing that as pH decreases, Cd uptake by plant increases; 2. cationic composition, as the uptake of Cd is frequently related to a decrease in the uptake of other essential elements, due to a competitive process (Mourato et al. 2019); 3. SOM, considering that the organic constituents, introduced through natural vegetation and farming form both soluble and insoluble complexes with Cd and, thereby, play a role in Cd transformation, have the ability to perturb the hydrolytic reactions of aluminium (Al) and the crystallization of their precipitation products; 4. the ratio of aluminosilicates/Al oxides, as these have specific adsorption sites for Cd ions induced by forming covalent bonds by the affinity of Cd for oxygen (Ramtahal et al. 2019); and 5. the genetic of cacao varieties (Lewis et al. 2018; Engbersen et al. 2019), because between varieties, the biotranslocation/bioaccumulation ratio may vary even if 'as species', *Theobroma cacao* L. has been classified as hyperaccumulator (Kirkham 2006).

Cd toxicity affects Ca, Mg, P and K input, transport and utilization (Haider et al. 2021). Looking at the role of macronutrients in Cd availability, other studies have reported that the abundance of Ca in acidic soils reduces Cd toxicity, mainly by reducing its uptake and competing with it at the transport site in the rhizosphere (Naeem et al. 2019). Regarding the same study, it was shown that Mg content can have a protective effect mainly due to the improved antioxidant status inhibiting Cd plant absorption. Another study (Nezhad et al. 2014) pointed out that high Cd concentrations in soils can be explained by the occurrence of magmatic rocks in the area, whereas areas characterized geomorphologically as alluvial deposits have the lowest altitudes within the region with lower heavy metal content. Interestingly, in the same study it was pointed out that Cd content was significantly positively correlated with sand and elevation ($r = 0.720$, $p < 0.01$). Therefore, assessing the spatial distribution of Cd taking into account the soil geology, climate, elevation, biomineralization and human activity, in both topsoil and subsoil, is critical for cocoa crop management and clean production.

However, the parameters above are not enough to explain the Cd soils/beans distribution in cacao systems with the complexity of edaphoclimatic conditions mentioned; therefore, it is necessary to come up with new non-destructive and highly sensitive techniques to assess these metal distributions. In the last decade, several techniques based on geophysical principles, for example, electrical resistivity tomography (ERT) were used for characterizing soil heavy metals distribution (Cuong et al. 2016; Benyassine et al. 2017).

A recent study has used ERT to study Cd soil distribution in cacao-growing farms from Colombia (Bravo and Benavides-Erazo 2020). Several correlations between high loads of specific heavy metals content (Cd, Pb, Al, Fe, Mn, Zn, Mo, V, Cr, Ni and Co) and electric response have been proposed (Abu-Zeid et al. 2004). For instance, the physicochemical characterization of phosphogypsum pond using geochemical and geophysical techniques based on ERT measurements allowed the prediction of the heavy metals spatial distribution through statistical models showing that the most concentrate metal is chromium with a maximum of ≈ 900 mg kg^{-1} and Cd is the least concentrated of maximum ≈ 23 mg kg^{-1} (Vásconez-Maza et al. 2021). Previous studies reported a decreasing tendency of resistivity with the increase of heavy metal ion concentrations (Zn^{2+}, Cd^{2+} and Pb^{2+}) in contaminated soils (Chu et al. 2017).

This technique has also been previously used to study mineralogical properties in agricultural subsoils (Domra Kana et al. 2015). The 2D-ERT technique is a low cost field data acquisition proxy to determine the spatial variability and distribution of physical properties of soils, such as soil structure, water content, soil contaminants and distribution of soil solutes, (Zhou et al. 2020) as shown in Fig. 1, where representative materials found in both solid-phase state and soil solution are located according to their resistivity values. The underground components respond differently to electrical currents generating an electrical contrast signal. The presence of some metals decreases the electrical resistivity values generating a significant electrical contrast with the background; that is why, heavy metals resistivity is a proxy for predicting soil contamination distribution (Vásconez-Maza et al. 2020). In the context of soil mapping, electrical resistivity exhibits a large range of values; for instance, from 1 Ω m for saline soils to 105 Ω m for dry soils overlaying crystalline rocks (Samouëlian et al. 2005). Interestingly, Cd content, after calibration, could also be observed in solid-phase Cd-like compounds in the assessed soil (Bravo and Benavides-Erazo 2020).

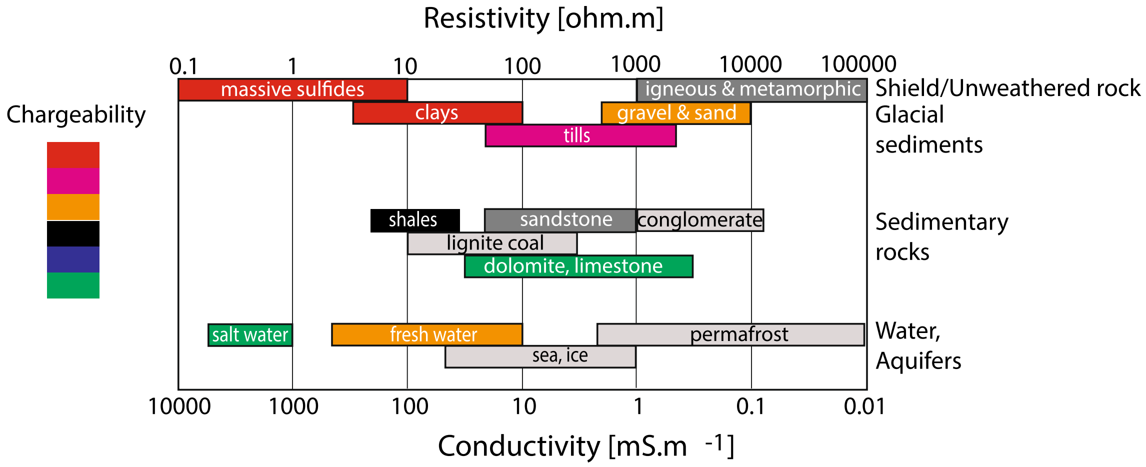


Fig. 1 The charge capacity of different material occurring in both natural and farming soils (modified from Samouëlian et al. 2005)

The 2D-ERT technique including other physics, chemical, biological and geo-statistic tools has demonstrated advantages in studying Cd in cacao fields, which includes 1. the analysis of several soil types with specific ratio of surface/subsoil, 2. assessing local variability of Cd content within the cacao farm, 3. having accurate measurements correlated with inductive coupled plasma (ICP) Cd counts and 4. yielding a cost-efficient diagnostic approach for farmers. However, both soil parameters and geologic features have just recently been included to assess the Cd flux integrated in a predictive manner.

Therefore, this is the first study that comprehensively integrates the Cd flux between soils and beans in cacao-growing farms in Antioquia. This research aims to determine Cd content in soils, soil litter and cacao beans, following the Cd fluxes within each cacao system using the 2D-ERT. The hypothesis of bioaccumulation of Cd, from both soil minerals and applied fertilizers, in cacao tissues and its release to soil surface at highly bioavailable forms by soil litter was evaluated. This hypothesis implies cadmium cycling within the system, which manifests as a thermodynamically 'open' system, where both the cacao varieties, the soil parameters (resistivity, effective CEC, electrical conductivity -EC, pH, SOM, Aluminium [Al], $Al^{3+}H^{+}$, Ca, K, Mg, and P content) and the geology and weather (mainly altitude) from every farm were assessed. This research study was carried out in cacao farms from the Antioquia´s Magdalena basin, in Colombia, between September 2019 and March 2020.

Materials and methods

Study area and sampling setup

This research was carried out in farms located in Antioquia's district, in the municipalities of San Roque and Maceo, which are part of the northeast region of the Antioquia's Magdalena basin. The location of the assessed farms is shown in Fig. 2.

Due to the protection of farmers, the farms assessed here were classified as farms A–D. The farms showed differences in productivity, cacao genetic varieties, age of culture, planting distribution, topography and agronomic management. The edaphoclimatic characteristics were contrasting, with an altitude ranging between 850 and 1113 m, temperatures ranging from 23 to 28 °C, annual precipitation ranging from 1500 to 2500 mm and relative humidity ranging from 7 to 80% (Martínez Covaleda et al. 2005; Pacheco-Montealegre et al. 2020).

Each farm had an average of 4 ha of cacao, within farms ranging from 2 to 70 ha. Sampling plots had an area of 2 ha and included 12 cacao trees. The cacao trees were identified and marked on their trunks to provide traceability of collected samples and monitoring individuals.

Farm A was located in the municipality of San Roque, in the sidewalk of San José del Nus at an altitude of 850 m, with an average temperature of 27 °C. The observed ground slope was ≥ 40%. The cacao varieties correspond to TCS01, TCS06, TCS13, TCS19 and CCN51, with an average age of 4 years.

Farm B was located in the municipality of Maceo, in the sidewalk of Betulia at an altitude of 1113 m and with a mean temperature of 24.1 °C. The plot was categorized by a slightly flat topography. The cacao varieties found were FSV41, FSV155, FCH8, FTA2 and CCN51, with an average age of 8 years.

Farm C was located in the municipality of Maceo, in the sidewalk of La Unión, at 990 m of altitude, with a temperature of 28 °C on average. The ground slope was > 50%. The cacao varieties found were FSV41, BETULIA8, BETULIA18 and BETULIA19, with an age of 5 years. It is worth mentioning that the 'Betulia' materials are from the group of 'creoles'; they have low adaptability to changing climate conditions, as they have been recognized with low vigour and high susceptibility to pests and diseases (López-Hernández et al. 2019). Nevertheless, they are known for their high quality due to them featuring large beans of white cotyledons that develop an adequate aromatic intensity during processing and roasting, with high content of chemical precursors of fine flavour (Avendaño-Arrazate and Cueto-Moreno 2018).

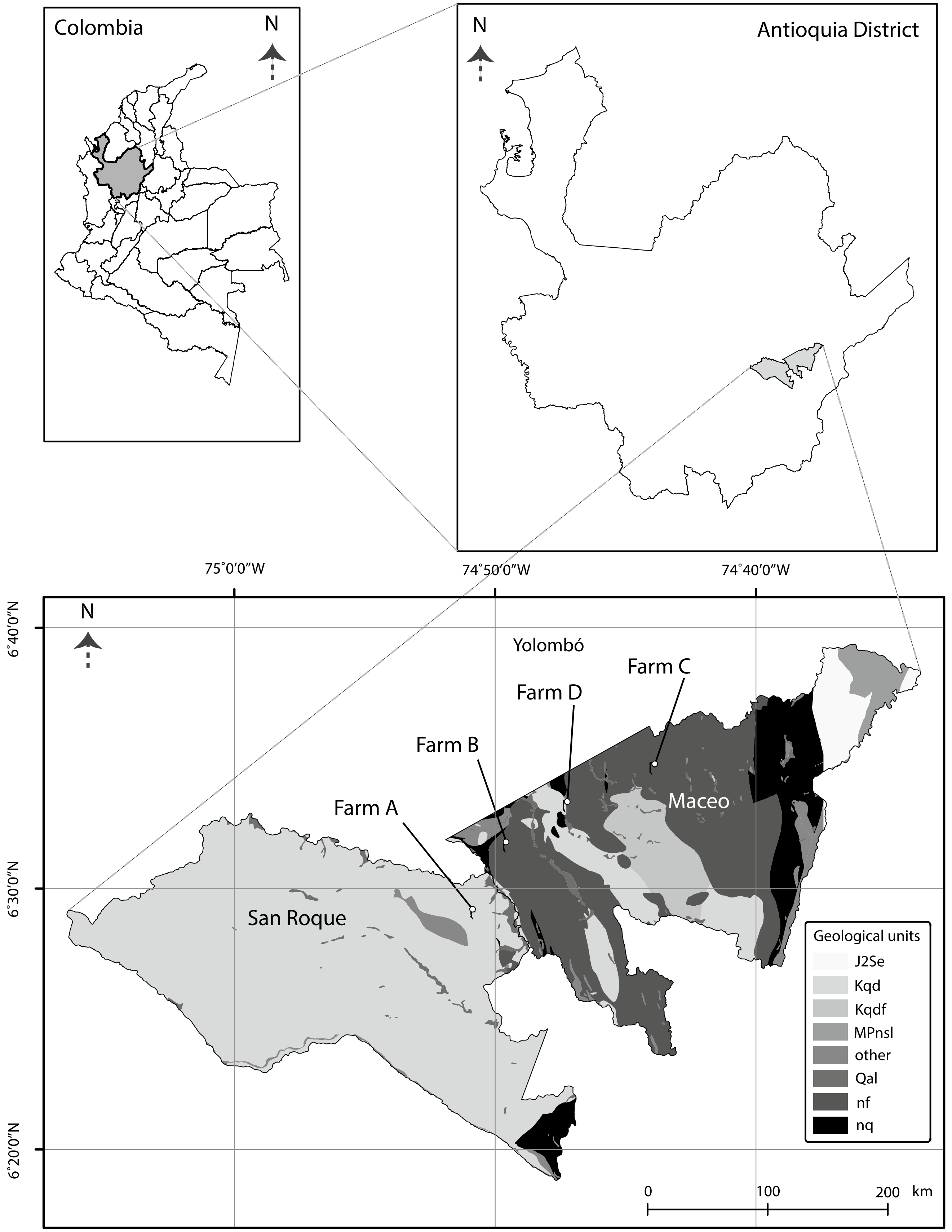
Farm D is located in the municipality of Maceo, in the San Luis sidewalk at 1058 m of altitude, with a mean temperature of 30.7 °C and with a ground slope ≥ 90%. The selected plot was established with the cacao varieties ICS95 and CCN51 with an age of 9 years on average. The CCN51 variety is considered a precocious tree of high quality and productivity, tolerant to diseases, with large pods and seeds and easy to handle since it does not reach great heights (Jaimes et al. 2017). Furthermore, the CCN51 genotype is currently the most commercialized variety in several countries, such as Ecuador, due to its high productivity (Santana et al. 2018).

Previous studies have reported differences in Cd allocation and bean accumulation between cacao cultivars (Arévalo-Gardini et al. 2017; Lewis et al. 2018; Engbersen et al. 2019). Nonetheless, the role, the impact based on the analysis of absorption and translocation effect of the genetic materials, which could play an important role in Cd distribution in cacao crops, was outside of the scope of this research.

Physicochemical analysis

To determine soil texture, a set of disturbed soil samples of 1 kg was sent to the Laboratory of Soils, from the Corporación Colombiana de Investigación Agropecuaria AGROSAVIA, in C.I. Nataima, located in El Espinal, Colombia. The soil samples were passed through different sieves using an automatic shaker for 5 min. The particle size was measured on air-dried soil < 2 mm following the methodology proposed elsewhere (Bouyoucos 1962) using a hydrometer (ASTM Soil Hydrometer 152H; Temp. 20 °C), after removal of carbonate with HCl treatment and organic matter with 30% H_2O_2.

Composite samples of soils of 1 kg each were collected under the cacao canopy of the sampling plots at a soil depth of 0–20 cm. The A boundary corresponds to the layer where the larger proportion of roots are located in cacao crops, as previously mentioned (Moser et al. 2010; Carr and Lockwood 2011). In farm A, three topsoil samples were collected both at the top and the bottom of the slope, one extra topsoil sample was collected in the middle of the slope, and three soil samples were collected a depth from the soil pit. In farms B, C and D, one topsoil sample was collected at both the top and the bottom of the slope, and two samples were collected from depths defined by the thickness of observed horizons differentiated by macro morphological characteristics in the soil pits. In all cases, the sampling distribution was defined by the arrangement of cacao clones within the plots. Samples of soil litter were collected from eight points following a zigzag path, to reach a final weight of 1 kg per sample. Fresh cacao seeds were collected from 3 mature fruits by variety in each farm. Soil samples, soil litter and cacao beans were stored at 4 °C and sent to the Laboratory of Soil Chemistry in the Corporación Colombiana de Investigación Agropecuaria AGROSAVIA, C.I. Tibaitatá, in Mosquera, Colombia, for chemical analysis. The soil samples were dried at 40 °C and sieved using a 2-mm size pore filter. The EC was determined with a conductometer electrode in soil/water solution (1:5 w/v), using the methodology proposed in a previous study (Richards 1954), with an electrode type conductivity sensor InLab 720 (Automatic Titrator T90, Mettler Toledo, Columbus, Ohio, U.S). The soil pH_{H2O} was determined by a potentiometric method in a soil/water solution (1:2.5 w/v) using the pH electrode InLab Max Pro, according to the standard method (Peech 1965). The SOM content was measured using the gold standard (Walkley and Black 1934) modified method, where soil was treated with potassium dichromate and twice the volume with sulphuric acid. Once the oxide reduction has occurred, the SOM was quantified using a UV–visible spectrophotometer (PerkinElmer spectrophotometer Lambda 25, Waltham, Massachusetts, U.S). The $Al^{3+}H^{+}$ was determined in a potassium chloride (KCl)-based soil extract solution which was titrated with sodium hydroxide (NaOH) 0.01 M by the titrimetric method (Coleman and Thomas 1967) using an Automatic Titrator T90 (Mettler Toledo, Columbus, Ohio, U.S). The Al content was determined using atomic absorption spectrometry -AAS (Agilent 280FS AA, California, United States) and dissolved in a KCl solution according to the classical method (Pratt and Bair 1961). The exchangeable cations Ca^{2+}, K^{+}, Mg^{2+} were extracted using a CH_3COONH_4 solution 1 M at pH 7.0 by the method proposed elsewhere (Shuman and Duncan 1990), where interchangeable bases are replaced by ammonium ion and the extracted elements


Colombia
N
Antioquia District
N
75°0′0″W
74°50′0″W
74°40′0″W
6°40′0″N
6°30′0″N
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Farm D
Farm B
Farm A
Maceo
San Roque
Geological units
J2Se
Kqd
Kqdf
MPnsl
other
Qal
nf
nq
0
100
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◀**Fig. 2** Geographical distribution of assessed farms. The farms were located in two geological units out of five reported in the Antioquia district. Geological abbreviation: *J2se*: Batolite of Segovia; *Kqd*: Intrusive rocks. Antioqueño Batolite. Cuarzodiorite; *Kqdf*: Phelsique Cuarzodiorite; *MPnsl*: Saint Lucas Kneiss; *Other*: Other rock geoforms; *Qal*: Alluvial quartz deposits; *nf*: metamorphic rocks from central cordillera located at the west of out fault. Feldespar aluminium kneiss, with migmatite and intrusive kneiss (ni); *nq*: quarzite, dark quartz biotite and quartz kneiss as part of the metamorphic complex in Central Cordillera. (Moya-Berbeo 2012)

were quantified using AAS. The CEC was calculated as the sum of the cations. The P content was determined by reduction with ascorbic acid using the Bray II method (Bray and Kurtz 1945), where the soil samples were treated with an extraction solution of ammonium fluoride in chloric acid (NH_4F 0.03 M-HCl 0.1 M), dissociating some phosphates from soil, due to the presence of NH_4F in the acid solution which make complexes with trivalent Fe and Al ions and releasing P content. The quantification of P was performed using the UV–visible spectrophotometer at 887 nm of wavelength. The samples with a P content below the detection limit for analytical measurement (Bray II) of 3.87 mg kg^{-1}, defined on the basis of the Eurachem Guide for measurement uncertainty (Ellison 2014), were not taken into account in the statistical analysis. The soil samples collected to determine the cadmium contents were previously pre-treated. The samples were oven-dried at 40 °C, and then, the samples were pulverized in a mill and sieved with a sieve of 0.5 mm of opening. The pseudo-total Cd content was obtained by digestion using nitric acid (HNO_3)-perchloric acid $HClO_4$ (9:3 v/v) in a heating plate to 160 °C under an extraction cabin, method modified in previous studies (Chavez et al. 2015; Bravo et al. 2018). The Cd content was measured using an inductive coupled plasma spectrometer with optical emission (ICP-OES) (Thermo Scientific ICAP 6000, Waltham, Massachusetts, US). Soil Cd content exceeding 0.5 mg kg^{-1} was considered evidence of soil contamination (McBride 1994). The soil litter for the Cd contents was pre-treated, washed using a solution of HCl 0.1 M and rinsed with deionized water for 30 s. The samples were dried in a stove at 68 °C for 48 h, and then, in a mill, the dry material was homogenized. For digestion o soil litter, 0.50 g of sample was digested with a solution of HNO_3–HCl_3O_4 (5:2 v/v) using a microwave digester (Milestone ultraWAVE, Sorisole, Bergamo, Italy), and the Cd content also was determined using the ICP-OES equipment. Cd in beans was quantified using the protocol reported in a previous work (Chavez et al. 2015). Briefly, the samples were dried between 70 and 80 °C for 24 h. The cacao beans were powdered and sieved using a 0.5-mm filter; 0.30 g of sample powder was digested in a solution of HNO_3–H_2O_2 (v/v), using a heating plate. The Cd determination in beans was also performed using the ICP-OES.

On each farm, the fertilization plan for the cocoa crop was consulted with the farmer owners to determine possible anthropogenic sources of contamination with Cd that was considered for analysis of the methodological setup. To analyse the chemical fertilizers, 500 g of each of the fertilizers used in the farms were collected to make a survey related to its chemical composition, type of packing (granulated or emulsified) and the method of application (soil or foliar). Also, the doses and frequencies of these products were requested to the farmers. The nutritional requirements of cocoa vary according to cultivars, crop conditions and, especially, with the degree of shading. The frequency of fertilization is given in two annual periods depending on the rains. Usually, the fertilization is carried out at the beginning and end of the rainy season (Álvarez-Carrillo et al. 2015). The sampling in all the farms was carried out during the month of November, two months after the fertilization process that traditionally takes place during the month of September corresponding to the rainy season in the study area.

Laboratory calibration of 2D-ERT

The calibration of the electrical resistivity was performed at the laboratory of Physics in the University of Nariño, Pasto, Colombia. To perform the calibration test, the ASTM D4700—15 method was used (ASTM 2012). Briefly, five concentrations of cadmium chloride ($CdCl_2$) were used to determine the resistivity of amended soils. The concentrations were 0.30, 0.60, 0.95, 1.50 and 2 mg kg^{-1} of the reagent ($CdCl_2$ Sigma-Aldrich, Chicago Illinois, US). Contaminated soil samples, collected from the excavation pits dug in the studied farms here assessed, were compacted in three glass containers of a cubic geometry with 4 mm thickness. Because the interest in this study was to determine the apparent electrical resistivity in the soil sample, it was essential to avoid procedures such as sieving or treatments to separate component materials (Mostafa et al. 2018). Fifty g of the samples was pressed to 50 ± 0.5 kPa and homogenized with each Cd concentration into the plastic cube moulds. The samples were compacted using a universal multi-test machine UTM-P (Ubique Systems, Maharashtra, India). (Bravo and Benavides-Erazo 2020). In each glass container, four electrodes were inserted at 0.01 m distance based on the Wenner method (Turki et al. 2019). For safety issues, the entire resistivity measurement process was carried out inside an extraction hood. Resistivity measurements were made using the resistivity meter UT523A (UNI-T, Hong Kong, China). The relation between soil resistivity values and soil Cd content was established at the laboratory, according to the ASTM G57-06 method, reported elsewhere (Domra Kana et al. 2015). The results of the standardization are shown in Table 1 as the standard deviation of the 60 lectures corresponding to each cadmium concentration.

Table 1 Standardization of electrical resistivity measurements in laboratory

Cd amended [mg kg^{-1}]	Electrical resistivity [Ohm m]*			
	Soil farm A	Soil farm B	Soil farm C	Soil farm D
Natural	‡515.12	‡2016.00	‡992.72	‡928.07
0.18	516 ± 7.76	2016 ± 16.86	990 ± 12.10	925 ± 11.81
0.37	517 ± 7.76	2017 ± 13.55	996 ± 11.25	939 ± 14.71
0.58	525 ± 5.79	2017 ± 14.26	995 ± 10.36	945 ± 11.62
0.92	528 ± 4.67	2020 ± 16.50	998 ± 10.63	946 ± 12.60
1.23	533 ± 3.04	2020 ± 14.07	999 ± 10.30	960 ± 12.52
R^2	0.95	0.89	0.63	0.83

*The ± symbol correspond to the standard deviation of the measurements

‡The electrical resistivity value was obtained from the first intersection point of the lineal regression

After achieving calibration with the five cadmium amendments, the linear regression was used to obtain electrical resistivity values when no cadmium amendment was performed. The first line in Table 1 shows the electrical resistivity counts determined with the lineal regression of the data when cadmium content is the 'natural' Cd occurring within the soil samples. A positive correlation between electrical resistivity and cadmium concentration has been observed and documented in previous studies, i.e. for low concentrations of $CdCl_2$ varying between 0.02 and 20 mg kg^{-1}, the resistivity is very high (Ayoub et al. 2003). Regarding the soil cubes amended with small amounts of Cd, the change of electrical resistivity values was consistent with the increasing Cd concentrations, even at low enrichments of $CdCl_2$.

2D-ERT field measurements

The resistivity tomography technique can provide a highly detailed information of the subsoil structural pattern based on high resistivity contrasts that characterize geological environments (Piegari and Di Maio 2010), as the primary objective of on-site geoelectric prospecting in both the topsoil and subsoil. On each studied farm, three prospecting lines were installed in parallel and separated by a distance of 1 m, in such a way that they were always transversal to the slope of the land, since the greatest interest lies in the exploration of soil boundaries close to the surface, which was achieved by applying the Wenner array method (Turki et al. 2019). Each line consists of 36 electrodes of high-quality stainless steel rods (AISI 316) of 0.005 m diameter and 0.4 m length. Electrodes were positioned in a straight line with 0.35 ± 0.02 m spacing, for a total line length of 12.2 ± 0.7 m. Nine resistivity levels were measured for a total of 198 points per Sect. 36 sections were linked together to achieve a full coverage per soil profile. Electrode spacing was selected in a way to reach 2 m of penetration depth which may provide information of Cd distribution. Apparent resistivity data (ρ_A) data were plotted in a pseudo-section. Once the geoelectrical profile was obtained, soil pits were dug to collect soil samples from the cacao subsoil, for both physicochemical analysis and standardization of the 2D-ERT technique at laboratory. The geoelectrical profile need to be converted into sections with true resistivity values and depths through a data inversion procedure to facilitate profile interpretation. For that, the Res2Dinv of Geotomo Software (Barker 1981; Loke et al. 2003) was used in the present study to process ρ_A data to real electrical resistivity data in the field. Data processing steps included removing bad data points by selecting the inversion method. Res2Dinv programme employs the inversion technique with a softness constraint to produce a 2D model of the ρ_A data in rectangular blocks. The depth of the bottom row of blocks is set to be approximately equal to the equivalent depth of investigation (2 m). The inversion routine used by the programme is based on the least square method with softness constraint (deGroot-Hedlin and Constable 1990; Sasaki 1992). The inversion model tomography was obtained using the robust data constraint option, which tends to produce models with a much sharper limit between different regions where different resistivity values may occur (Loke et al. 2003, 2014). The field tomography of the three lines was generated. Based on them, the sector with the highest contrast of resistivities was located, also called anomalies, determining the length and depth of sampling points.

Data analysis

Data analysis was performed using R Project 3.6.2 (R-Core, 2019). A Pearson correlation analysis was carried out with the '*Hmisc*' software package (Harrell 2017), including the variables of Cd content in soils, soil litter, cacao beans, the farm altitude, the age of the crop and 10 soil parameters: CEC, EC, pH, SOM, Al, $Al^{3+}H^{+}$, Ca, K, Mg, and P content. In addition, a principal component analysis (PCA) was performed with the '*stats*' and '*ggbiplot*' packages for R software (Vu 2011), applying the same parameters used to perform the correlation analysis. Only the P content was not taken into account because the values were below the threshold. To compare the Cd content in both soil and beans, a Kruskal–Wallis test and a Conover multiple comparisons test were performed, using the '*agricolae*' package for R software (de Mendibru 2017). To determine the best predicting variables to Cd contents in cocoa beans, a backward stepwise regression analysis was conducted including soil and environmental variables without logarithmic transformation taking into account the number of samples. The test was performed using the '*caret*' package to R statistics

Table 2 Chemical properties of soils in studied in cacao farms

Farm	Position*	Depth [cm]	pH	EC [dS·m^{-1}]	SOM [%]	CEC [cmol$_+$ kg^{-1}]	Ca	Mg	K	AlH	Al	P [mg kg^{-1}]	Cd$_s$	Cd$_b$
A	Topsoil ↑	0–20	5	0.22	2.83	3.02	1.77	0.73	0.12	0.33	0.1	< 3.87	1.54	1.44
A	Topsoil ↓	0–20	6.74	0.41	3.28	12.65	9.88	2.47	0.23	0	0	< 3.87	1.61	0.96
A	Topsoil ↑	0–20	7.01	0.42	3.59	14.19	11.72	2.12	0.28	0	0	< 3.87	1.8	0.84
A	Topsoil ↔	0–20	5.36	0.3	4.05	4.28	2.97	0.81	0.3	0.12	0	< 3.87	1.66	0.62
A	Topsoil ↓	0–20	4.93	0.32	3.63	3.82	2.18	0.63	0.41	0.52	0.34	< 3.87	1.74	–
A	Topsoil ↑	0–20	6.74	0.35	2.89	11.83	9.39	2.18	0.16	0	0	< 3.87	1.71	0.65
A	Topsoil ↓	0–20	5.62	0.34	3.56	5.62	4.34	1.07	0.14	0	0	< 3.87	1.72	0.75
A	Underground	100–120	5.06	0.12	0.7	1.73	1.02	0.51	0.09	0.1	0	< 3.87	1.76	–
A	Underground	58–78	5.18	0.14	1.01	1.51	1.11	0.28	0.09	0.03	0	< 3.87	1.76	–
A	Underground	21–41	4.86	0.13	2.18	1.67	0.89	0.27	0.09	0.37	0.21	< 3.87	1.66	–
B	Topsoil ↑	0–20	5.94	0.27	3.62	9.33	7.34	1.69	0.2	0	0	14.5	1.99	0.09
B	Topsoil ↓	0–20	5	0.21	3.48	4.8	3.07	0.4	0.09	1.17	0.84	10.31	1.87	0.11
B	Underground	50–70	4.68	0.06	1.34	2.68	0.59	0.2	0.09	1.98	1.71	< 3.87	2.02	0.11
B	Underground	10–30	4.79	0.2	2.99	4.08	1.82	0.61	0.13	1.43	1.03	< 3.87	2.03	0.14
C	Topsoil ↑	0–20	4.76	0.37	3.23	6.42	2.44	0.94	0.13	2.83	2.3	< 3.87	1.53	0.11
C	Topsoil ↓	0–20	4.7	0.27	3.9	7.09	3.1	0.87	0.14	2.9	2.31	< 3.87	1.45	0.08
C	Underground	90–110	4.98	0.03	1.01	1.94	0.59	0.2	0.09	1.4	1.19	< 3.87	1.66	0.08
C	Underground	28–48	4.58	0.15	2.31	4.35	0.59	0.23	0.13	3.38	3	< 3.87	1.57	0.12
D	Topsoil ↑	0–20	5.09	0.18	2.84	3.76	1.99	0.87	0.24	0.57	0.27	6.73	1.33	0.13
D	Topsoil ↓	0–20	5.02	0.16	2.51	3.71	1.69	0.73	0.4	0.81	0.5	< 3.87	1.29	0.21
D	Underground	85–105	5.09	0.05	0.6	2.45	0.59	0.55	0.09	1.41	1.05	< 3.87	1.62	–
D	Underground	9–29	4.96	0.21	2.32	3.49	1.75	0.96	0.14	0.56	0.27	< 3.87	1.22	–

*Position in the hill slope: ↑ Top; ↔ Middle; ↓ Bottom

Cd$_s$: Cd in soils; Cd$_b$: Cd in beans; ND: No data

(Kuhn et al. 2020). The variables were selected based on the maximization of adjusted R^2 and minimization of Root Mean Square Error or *RMSE*. Statistical significance was considered at a P value ≤ 0.05.

The 2D-ERT calibration was done on a laboratory scale. The collected information was statistically processed using a CERN's ROOT data analysis framework and ORIGIN 8 to determine the initial apparent electrical resistivity, which is given in Ohm per meter (Ω m). Processing and interpretation of the measured resistivity data were performed using the 2D finite difference inversion programme (Loke 1999).

2D-ERT predictions

The tomograms were redefined according to a grey scale following a previous methodology (Bazin and Pfaffhuber 2013). Briefly, the chromatic values of the 'standard' tomography were conversed to grey scales, where light–weak colours corresponding to low resistivity values were represented in low grey scales; meanwhile, dark–strong colours corresponding to high resistivity values were left in yellow to better notice its distribution (Metwaly and AlFouzan 2013). Therefore, the range of resistivity values corresponding to the measured Cd counts from the laboratory calibration process for each farm is highlighted avoiding the noise of surrounding non-Cd-like compounds. This is derived from predictive tomography, because it indicates the most likely route of distribution of Cd or solid-phase Cd-like compounds across the underground assessed section in four vectors.

Results and discussion

Soil parameters

The soils of farms A–D, exhibit acidic pH, with values ranging from 4.58 to 7.01; the average value in A, B and D was ≥ 5 units. In farm C, a higher acidity with a pH of 4.75 on average was found, accompanied by a higher Al^{3+} and interchangeable acidity content (Table 2). The SOM of 3.1% was very similar to all farms assessed at the soil surface (0–20 cm depth). Farm D has the lowest SOM content, with 2.55% on average. Low CEC was observed with 5.2 cmol$_+$ kg^{-1} on average and low-medium Ca^{2+}, Mg^{2+} and K^+ contents were observed. The highest Ca^{2+} content was found

Table 3 Textural analysis of soil samples collected in the four cacao farms from Antioquia, Colombia

Farm	Soil sample depth [cm]	Textural classification
A	21	Clay-loam
A	58	Clay
A	100	Silty-clay
B	10	Clay-loam
B	50	Clay
C	28	Clay-loam
C	90	Clay
D	9	Sandy-clay-loam
D	85	Clay-loam

in farm A, where a maximum value of 9.88 $\text{cmol}_+\ \text{kg}^{-1}$ was found. The Mg^{2+} and K^+ contents were similar in the assessed farms with averages of 0.88 and 0.17 $\text{cmol}_+\ \text{kg}^{-1}$, respectively. Phosphorus content was below the threshold of 3.87 mg kg^{-1}. Farm B has the highest phosphorus content with 8.13 mg kg^{-1} on average, which continues to be a low level, according to the average thresholds for agricultural soils intended for cocoa cultivation (Snoeck et al. 2016). In the assessed farms, the soil Cd content ranged from 1.22 to 2.03 mg kg^{-1}.

Soil samples for texture analysis were collected at different depths for each farm according to the distribution and thickness of observed horizons, based on macromorphological characteristics (colour, structure; data not shown) studied within soil pits. This was corroborated when observing the depth of electrical resistivity anomalies in the geoelectrical profile from four farms. The soil textural analysis shows a predominance of clay at a depth ranging from 10 to 85 cm, as shown in Table 3. An increase in clay content with soil depth was observed at all of the studied farms. This can be explained by soil evolution and taxonomy as all the studied soils belong to the subgroup *Oxic Dystrudepts* (IGAC 2015). This means that the soil is classified as an Inceptisol, characterized by the presence of a Cambic horizon, but having an extragrade condition determined by the illuviation of clay from the upper horizons, conferring certain characteristics of an Oxic subsurface horizon (Staff 2014).

Cd in soils and cacao beans

The Cd content for both soils and beans is shown in Table 4. Farm B shows the major soil Cd content, with 1.98 mg kg^{-1} on average, followed by farm A with 1.70 mg kg^{-1} and farms C and D without significant differences between them. To farms B, C and D, the Cd content in cacao beans was below the critical level of 0.60 mg kg^{-1} defined by the European Union (European Comision 2014) for cocoa powder. On the contrary, beans Cd content in farm A ranged between 0.62 and 1.44 mg kg^{-1}.

The soil litter Cd content was 0.43, 0.61, 0.85 and 3.34 mg kg^{-1} in farms C, B, D and A, respectively. In farms B–D, the Cd contents decrease in the order of soil > soil litter > beans. In farm A, the average Cd content was higher in the soil litter, followed by soils and beans.

Interestingly, from the evaluated variables, only percentage of clay in the soil was significantly correlated with soil Cd content (0.69; P value < 0.05). Soil texture was not correlated with bean Cd content (see supplementary Table S2). However, the beans' Cd content has a highly significant correlation (P value < 0.01) with the soil litter Cd content (0.91), the altitude of the farms (− 0.82) and the age of the crop (− 0.62). It is noticed that due to the low number of farms evaluated (N = 4) these results must be validated for a district overview. A medium significant correlation (P value < 0.05) of the Cd content in beans was found, with the soil pH values (0.53), electrical conductivity (0.50), Al content (− 0.59) and interchangeable acidity (− 0.60). A low correlation (P value < 0.1) was found between the beans Cd content with Ca and Mg contents (0.45 and 0.49, respectively). It is highlighted at this point that the correlation

Table 4 The test of Conover for multiple comparisons was applied previous the analysis using the Kruskal–Wallis test for Cd content in both cacao beans and soils from the studied farms

Cd origin	Farm	Mean [mg kg^{-1}]	Min	Max	Mean rank	
Cocoa beans	A	0.88	0.62	1.45	13.50	*a**
	B	0.11	0.09	0.14	5.75	*bc*
	C	0.10	0.08	0.12	3.50	*c*
	D	0.17	0.13	0.21	9.00	*b*
Soils	A	1.70	1.54	1.80	12.90	*b**
	B	1.98	1.87	2.03	20.50	*a*
	C	1.55	1.45	1.66	6.75	*c*
	D	1.37	1.22	1.62	3.75	*c*

[**] Letters indicate the observed significant differences between Cd content in soils or cocoa beans in the assessed farms, using a 95% confidence level

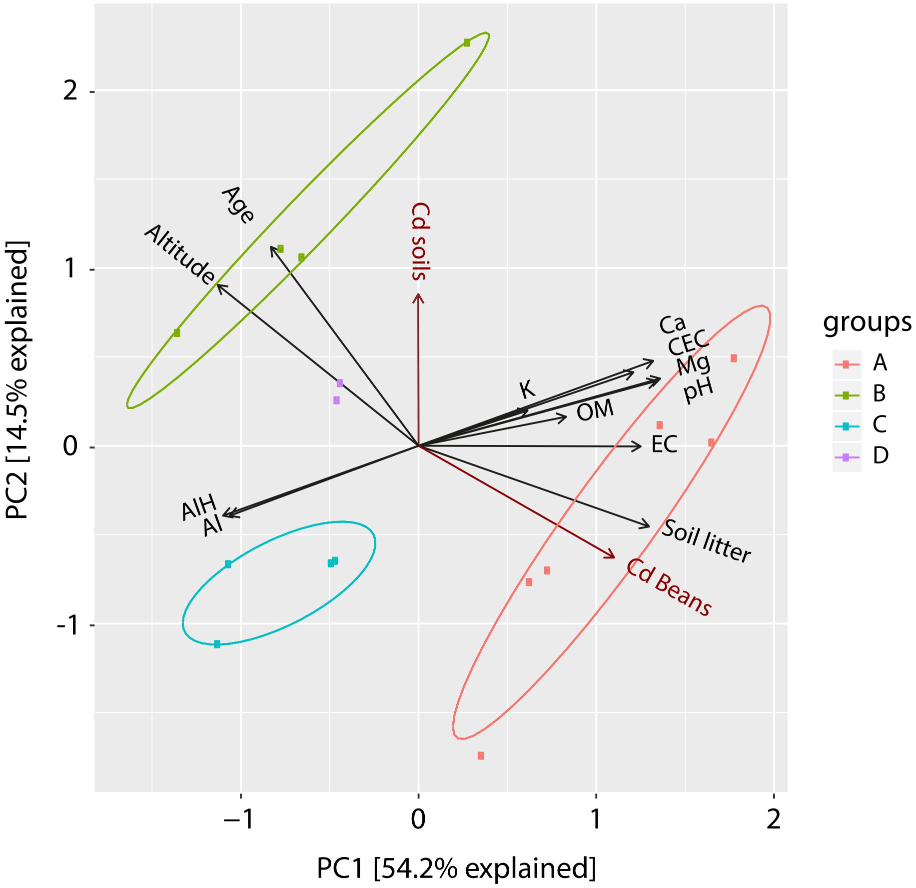

Fig. 3 A PCA biplot showing the PC1 and PC2. The PCA analysis was performed using soil parameters and productive parameters of the cacao-growing farms assessed in this study. The ellipses represent the variable dispersion in farms A–D, located at the municipalities of Maceo and San Roque in the Antioquia northwester district from Colombia

between the Cd content of soils and beans was not significant at this site-specific condition.

The PCA results are shown in Fig. 3. The first three principal components (PC) explain 80.2% of the total variability of the soil parameters. The PC1 represents 54.2% of total variance and is related to soil reaction. The highest coefficients are associated with variables such as pH (0.333), EC (0.306), Ca (0.323), Mg (0.328) contents, and the soil litter Cd content (0.318). The PC2 explains 14.5% of the variance and is related to the cacao crop and soil Cd content. The highest coefficients were associated with the age of the crop (0.530), the altitude of the farm (0.429) and the soil Cd content (0.404). The PC3 explains 11.4% of the variance and is related to the acidity of soils. The highest coefficients were associated with the Al^{3+} (– 0.487) content and the interchangeable acidity ($Al^{3+}H^{+}$) (– 0.466). Each of the remaining PCs represents less than 10% of the total variability (supplementary data in Table S1).

The graphic representation of PC1 and PC2, which together sum up 68.7% of the total variance of the data, shows specific relationships of certain variables with the farms analysed (see Fig. 3). Farm A is associated with high Cd content in soil litter and cacao beans, whereas farm B is more associated with the highest age of the crop, altitude and soil Cd content. In farm C, the variance of data is associated with the presence of Al^{3+}, low CEC and low Cd contents of soil, soil litter and cacao beans; meanwhile, in farm D there are half-conditions between farms B and C.

Based on the stepwise linear regression analysis carried out with the variables measured in farms A–D, it was found that the beans Cd content could be estimated by the interchangeable acidity ($Al^{3+}H^{+}$) and the altitude of the farm with an adjusted $R^2 = 0.72$, according to [Eq. 1]:

$$\text{Bean Cd}\left(\text{mgkg}^{-1}\right) = 3.009 - \left(0.1183 * \text{Al}^{3+}\text{H}^{+}\right) - (0.0025 * \text{Altitude}) \quad (1)$$

On the one hand, Eq. 1 indicates that, for the assessed farms, bean Cd content decreases by a factor of 0.118 mg kg^{-1} when each unit increases in interchangeable acidity ($Al^{3+}H^{+}$ $cmol_{+}$ kg^{-1}), at a constant altitude. On the other hand, the application of Eq. 1 indicates also that beans Cd content decreases 0.00253 mg kg^{-1} for each unit increasing in altitude, when the interchangeable acidity is constant.

The calculated beans' Cd content using the Ec. 1 was in a range of – 0.04 to 0.86 mg kg^{-1}, while the actual beans

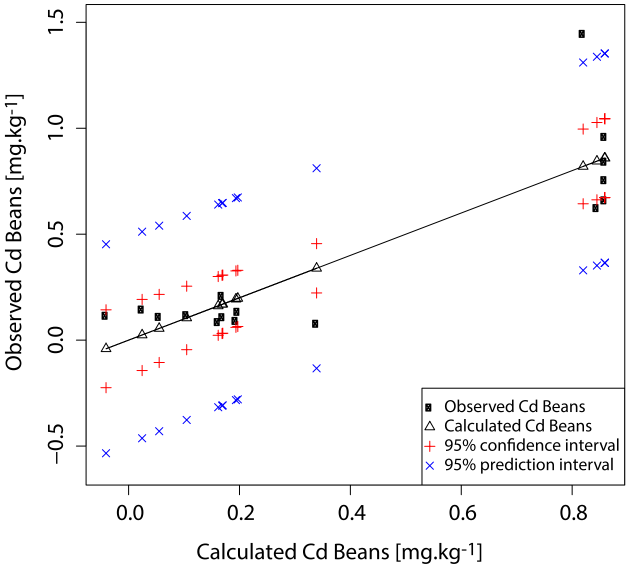

Fig. 4 Calculated Cd content vs. observed Cd content in fresh beans collected in the four farms assessed in this research. The coefficient of correlation adjusted $r^2=0.72$

Cd content was between 0.08 and 1.44 mg kg^{-1}. As shown in Fig. 4, only the observed value of 1.44 mg kg^{-1} of bean Cd content is outside the confidence interval (95%) and the prediction interval of the model. The maximum value estimated by the model barely exceeds the maximum content of Cd established at 0.8 mg kg^{-1} by the European Union and *Codex Alimentarius* for chocolates with ≥ 50% of cocoa (European Comision 2014; FAO/WHO 2018).

2D-ERT profiling

The 2D-ERT tomography of the assessed farms is shown in Fig. 5. Three lines were generated for each farm. Once the first geoelectrical profile was generated, soil pits were excavated when ERT did show contrasting properties in the subsoil. In this study, these points corresponded to high resistivity values represented by dark colours (from red to violet). A widespread distribution of soil Cd content was observed. Soil samples collected from the pits showed higher Cd content than the threshold value established for contaminated soils (Table 2).

The resistivity values of farm A showed great variability between 6.73 and 5020 Ω m (see Fig. 5a). Changes in resistivity values of soil surface were observed between the electrodes 16–20, which corresponds to 4.8–6 m of soil distance, at a depth of 0.4 m and between the 24–28 electrodes which corresponds to 7.2–8.4 m in soil distance, at a depth of 0.2 m, where there is a highly saturated material having a very low resistivity, with values between 8.78 and 20.3 Ω m. The possible cause of this is due to water retention with the consequent formation of salts, water retention potential or higher water table indicator. After the pit excavation, six types of constituent material were detected, which was distributed in three observed strata. At a depth between 0 and 0.40 m, the strata were seen to be disturbed by anthropic activity.

In the same way, three non-uniform boundaries were observed in their distribution and rather with highly altered strata. The tomography showed a conglomerate of materials with resistivities of 17.1–517 Ω m at a depth of 0.55 m. Between electrodes 4–11, which corresponds to the soil distance between 1.12 and 3.3 m and as a tank, at a depth of 0.6 m to more than 0.60 m, a material with a resistivity of 517 Ω m was observed. According to Fig. 1, that material could correspond to calcites or sandstones.

In the 2D-ERT tomography of farm B (Fig. 5b), two highly saturated zones were observed between electrodes 2–7 which represents the surface distance between 0.6 and 2.1 m, and electrodes 13–26 which corresponds to 3.9–7.8 m in soil surface, with a depth of 0.2–1 m, which could be related to saturated silty material or clay sands separated by a high resistivity material, of 1132 Ω m, such as consolidated sand-clay or limestone. An outcrop of material with resistivity > 2314 Ω m was observed. In Fig. 5b, it was observed between the electrodes 15–20 which corresponds to a surface distance between 4.5 and 6 m, and at a depth of 10 cm the existence of a compacted material with greater consolidation or rocky with a resistivity of more than 4731 Ω m, which probably corresponds to granites and stoneware from alteration in the recent soil formation. It is also noticed that the soils boundaries were combined or altered, probably due to an anthropogenic action, as described previously. The most superficial soils and their resistivity values of 133–271 Ω m indicate loam-type materials and saturated clayey silt.

In the tomography of farm C (Fig. 5c), the combination of different types of materials is observed in the profile of measured apparent resistivity, indicating layers altered by anthropogenic activity. Between electrodes 12–22 (corresponding to 3.6–6.6 m in soil surface distance) and at a depth of 0.4 m, there is highly saturated material with resistivities of 15.4–34.5 Ω m. Between electrodes 16 and 18 (which corresponds to 4.8–5.4 m in soil surface distance), outcroppings of high resistivity material 4425 Ω m are observed due to the presence of limestone or consolidated clay sands. There is no evidence of the presence of objects with very high resistivities, undercuts or the presence of groundwater, although in theory, low resistivity values are due to a high level of water in the ground, as the water is characterized by high electrical conductivity.

In the tomography of farm D (Fig. 5d), due to the complex topography of the assessed soil, it was possible to determine three boundaries with a certain degree of alteration, according to the levels of resistivity. The first boundary of 7.74–135 Ω m corresponded to saturated silt or loam,

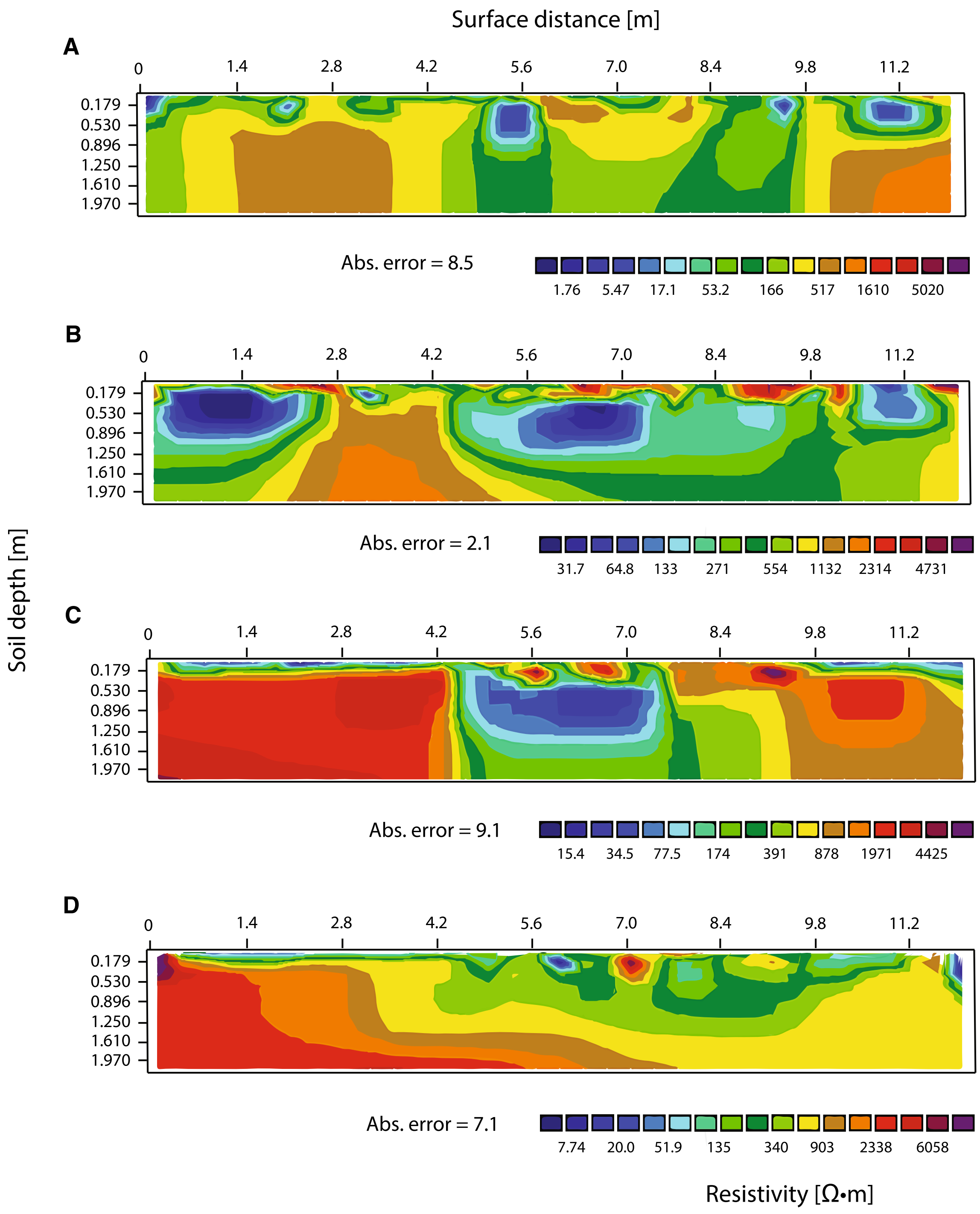

Fig. 5 The 2D—ERT inverse model resistivity section plots of farms in Antioquia. **a** Municipality of San Roque, farm A **b** Municipality of Maceo, farm B and **c** Municipality of Maceo, farm C and **d** Municipality of San Roque, farm D

followed by another layer between 135 and 348 Ω m, at 0.896 m, which corresponds to the particulate material with spots of SOM with resistivity values between 18 and 425 Ω m. The second horizon was presented at a depth of 0.9–1.43 m, with resistivities between 425 and 935 Ω m, which corresponds to typical values of muddy silt or saturated clay loam. The third horizon at a depth between 1.43 and 1.79 m, with resistivities between 935 and 2054 Ω m, corresponded to the loamy-sandy texture. In the first boundary (0.2 m soil depth), granitoid inlays with resistivities between 2054 and 4512 Ω m were observed, as in subsoil (1.79–1.97 m depth). This soil was characterized by registering low resistivity values due to its higher water content, and regarding the tomography, also due to compaction from 0.80 m. There was no evidence of the presence of solid-state phase content with very high resistivities. Regarding the surface to 0.8 m depth, resistivities correspond to typical texture of sandy-clay soils with a sand component observed in a spot of soil with a resistivity between 2054 and 4512 Ω m.

2D-ERT predictions

The previous tomography was redefined chromatically according to a grey scale (Bazin and Pfaffhuber 2013), compiling 1. the chemical analysis of Cd content, 2. the values of electrical resistivity measured during standardization (data not shown), and 3. the resistivity values that were obtained during the trial field. Figure 6 shows the predictive 2D-ERT profiles. As mentioned before, light grey colours were assigned to low resistance values and

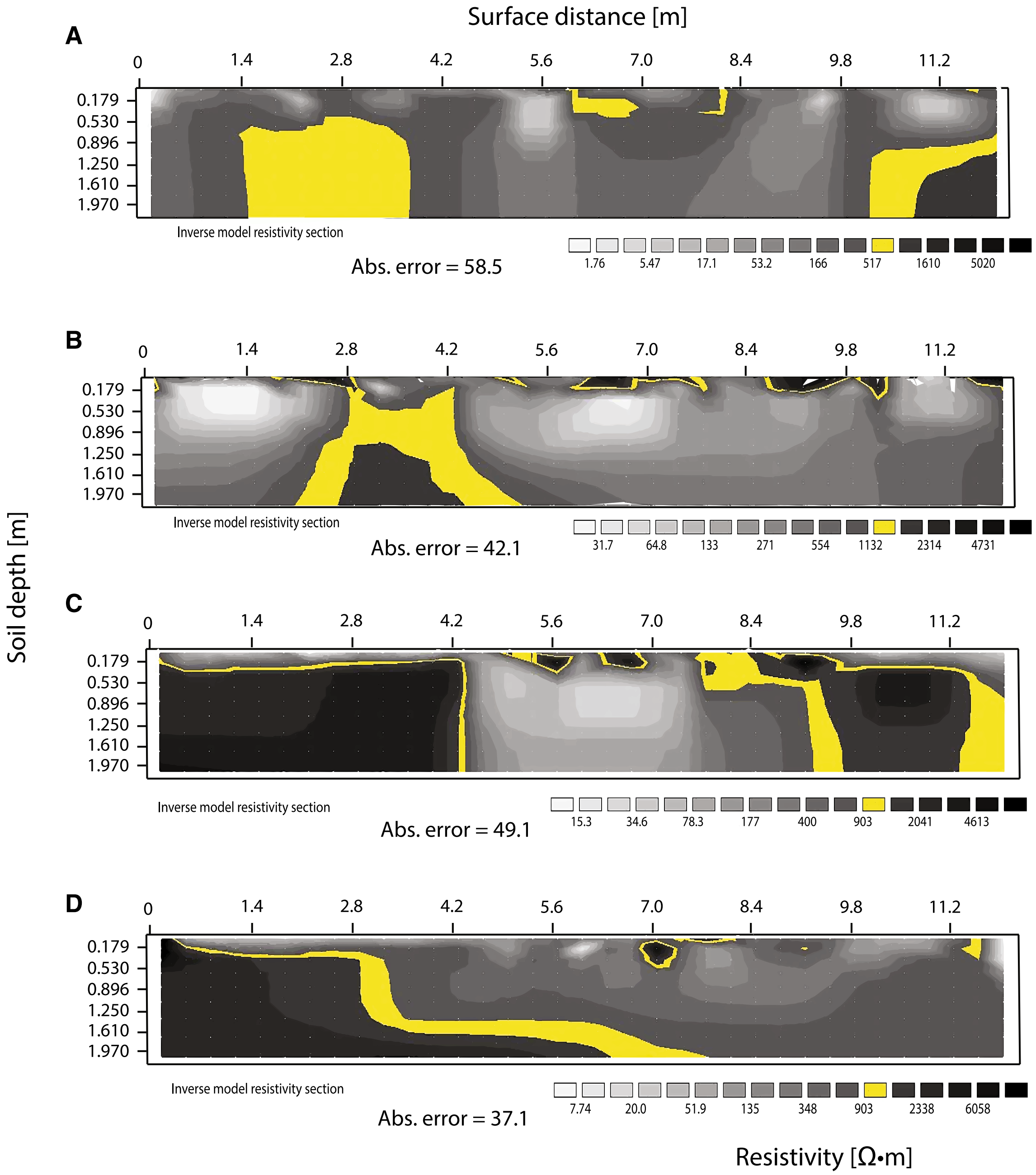

Fig. 6 Predictive 2D-ERT plots, using the inverse model section plots, belonging to the assessed farms in Antioquia. **a** Municipality of San Roque, farm A **b** Municipality of Maceo, farm B, **c** Municipality of Maceo, farm C and **d** Municipality of San Roque, farm D

dark grey colours to high resistivity values. The yellow colour was assigned to the range of electrical resistivity values corresponding to Cd content, as used in a previous work (Metwaly and AlFouzan 2013). The result was predictive tomography, which indicates the most probable route of distribution of Cd-like compounds.

This analysis was achieved once the initial tomography was determined. To each farm, the predictive models were assessed from the iterations of the resistivity inverse model.

In farm A, a large amount of soil litter and cacao pod husk was found with saprophytic activity and the release of organic carbon around the cacao trees. The Cd content was 1.70 mg kg^{-1} which correlate to a resistivity value of 515.12 ± 5.8 Ω m on average (see Fig. 6a). In this farm, there were a block formation of materials close to Cd resistivity with a horizontal extension from 1.40–3.85, 5.95–7, 8.05–8.40 and 10.15–12.6 m in the soil surface distance, some of them reaching the tail of the profile in underground. In that section of the tomogram, the direction of the Cd-enriched compounds is perceived to go from the surface to the subsoil.

In farm B (Fig. 6b), a great amount of soil litter and pod husk were observed on the surface of the profile. In this farm, an average Cd value was found in soils of 1.98 mg kg^{-1} associated with a resistivity of 2016 Ω m on average. The predictive 2D-ERT showed a distribution of Cd-like compounds from the surface to the centre of the pit, between 1.75 and 2.80 m and extending to 5.25 m. Some blocks with Cd-like material were observed in the topsoil, at 0.2 m depth. These blocks exhibit a horizontal extension in the range 4.9–5.6, 5.95–8.05, 8.75–10.5 and at 11.55 m in soil surface distance, which also showed a sense of expansion from the topsoil to the underground.

In farm C (Fig. 6c), less soil litter and pod husk were observed on the surface. The farm has 1.55 mg kg^{-1} on average of soil Cd content within the ERT profile, which was well correlated to a resistivity value of 992.72 ± 97 Ω m on average. As seen in the predictive tomography of Cd-like compounds (Fig. 6c), there is a mobility of the metal from the surface, superficially covering a material with higher resistivity, at a depth of 0.35 m. The dispersion of the enriched materials follows a horizontal distribution between 0 and 4.5 m and then continues vertically towards the soil profile. There are two zones forming blocks with a contour of Cd composite material very close to the surface, between 0 and 0.2 m deep and horizontally between 4.9 and 7 m of surface distance. Two continued intrusions that start in topsoil and move towards depth (2.1 m) are also highlighted, extending in two dimensions. The first is between 7.7 and 8.4 m and the second distributed between 8.75 and 12.6 m surface distances.

In farm D (Fig. 6d), the soil Cd content was of 1.37 mg kg^{-1} on average, which corresponds to a resistivity value of 928.1 ± 12.2 Ω m on average. Regarding the predictive ERT of the most probable distribution of soil Cd (Fig. 6d), three blocks of particulate material with resistivities close to Cd content were also observed. The blocks were observed at the Ap boundary, in the range 6.65–7.35, 7.35–8.40 and 11.55 m in the soil surface distance of the performed profile. All were located in the topsoil.

Soil parameters and its relation to Cd distribution

The soil Cd content of the assessed farms ranged from 1.22 to 2.03 mg kg^{-1}, reaching levels above a threshold for natural or uncontaminated soils of 0.5 mg kg^{-1} (McBride 1994). As previously mentioned, the soil Cd content has no correlation with Cd found in beans. Previous studies have described high correlations of soil Cd with beans Cd contents, both in Ecuador (Chavez et al. 2015; Argüello et al. 2019) and in Honduras, where the soil available Cd content, determined by the thin layer diffusion gradients (DGT) technique, was the best predictor of Cd content in cocoa beans, followed by pseudo-total soil Cd content (Gramlich et al., 2018). However, average values of Cd in cocoa beans exceeding the limit of 0.80 mg kg^{-1} proposed by the European Union (European Comision 2014) have been reported in places where the soils show low Cd contents, less than 0.43 mg kg^{-1} (Gramlich et al. 2018; Argüello et al. 2019).

Regarding the positive correlation observed between Cd content in soil litter and cocoa beans, it has been reported that the decomposition of soil litter might come up as an important source of bioavailable Cd on the soil surface (Gramlich et al. 2018; Maddela et al. 2020), as corroborated in Ecuador with the isotopic Cd fractionation (Barraza et al. 2019). According to our data, the positive correlation observed between soil pH and beans Cd content contrasts with previous reports (Argüello et al. 2019; Barraza et al. 2019), where increasing concentrations of Cd in beans occur with a decrease in soil pH. It has been highlighted that pH is the most influential factor in the availability of Cd to migrate from soils to the plant, since the strength of the cations' adsorption in soil surface increases at an acidic pH (Christensen and Haung 1999).

The model showed in Ec.1 features an interesting applicability in cocoa-producing regions which might be confirmed by further studies using a larger number of farms, including environmental variables such as the altitude and the age of the crop, that will improve the understanding of Cd fluxes and have not been considered in other related studies. In this study, when the beans Cd values increased, the error has been found greater, as in the farms here assessed, the predicted values were in the range of 0.04–0.86 mg kg^{-1}. Interestingly, other studies have reported levels of up to

10.4 mg kg^{-1} (Argüello et al. 2019), 9.6 mg kg^{-1} (Vanderschueren et al. 2020), 7.1 mg kg^{-1} (Gramlich et al. 2018), 3.92 mg kg^{-1} (Barraza et al. 2019) and 3 mg kg^{-1} (Chavez et al. 2015), in beans Cd content. Therefore, in other regions with higher beans Cd counts, a modification should be made. Likewise, the negative relationship of interchangeable acidity with beans Cd content was shown in Ec. 1 contrasts with previous studies (Christensen and Haung 1999; Argüello et al. 2019; Barraza et al. 2019) that reported a positive correlation between acidity and Cd bioavailability. The results of this study could be due to the fact that 86% of the soil samples have an acid pH between 4.58 and 6.5 units, where a significant percentage of available Cd might occur in a bioaccumulation frame of 4–8 years of cacao varieties established in the assessed farms. The 14% of the samples had a pH close to neutrality between 6.5 and 7.1. Some studies have analysed the correlation of soil Cd content with pH, CEC and content of clays (Chavez et al. 2015), Zn (Maddela et al. 2020) and Fe, K and Mg, showing high correlation with Fe (Bravo and Benavides-Erazo 2020) and low correlation with Mg and K (Gramlich et al. 2018). Furthermore, it has been reported that total soil Cd content and pH are the best explaining factors to accumulation of Cd in beans, while other variables such as SOM and the content of extractable—oxalate Mn increases the predictive power (Argüello et al. 2019). However, we would like to make aware of the differences between total soil Cd and beans Cd contents. The amount of available Cd in soils that cacao plants uptake may differ considerably, and it is lower than the total soil Cd content. This is due to, in part, Cd ions forming ligands with aluminosilicate compounds, after the isomorphic substitution of Al, Mg or Si, or because it could be found hydrated fully or partially and adhered to clay surfaces or to organic matter. The small fraction could be associated with hydrated cations available in the soil solution (Dharma-Wardana 2018). Such chemical complexation would explain the lack of correlation between soil and bean Cd content observed in this study. The determination of micro-elemental composition of soil, which was not measured in this study, or other factors such the Cd-tolerant bacteria (CdtB) that might affect the availability of Cd in soils, should be also considered in order to have a deeper overview of Cd dynamics. Nonetheless, an important input of Cd to the cacao system, as mentioned in this manuscript, is the application of chemical and organic fertilizers, which could reveal some of these relationships in the soils of Antioquia. As discussed later, the data show a possible intrusion of Cd into the cacao system with an anthropic contamination source, which, as a function of time, is generating a gradient of Cd availability.

The negative relationship between beans Cd content and the altitude of the studied farms (Ec. 1, Fig. 4) could be associated with a low scale geological differences that cannot be observed on the geological overview of Fig. 2, due to its large scale of 1:100.000 (Gómez et al. 2015). However, it is pointed out that cacao-growing soils in Antioquia exhibit high geodiversity featuring igneous, metamorphic and sedimentary rocks as possible parent material (Rendón Rivera et al. 2013), which differs in Cd content (Traina 1999). The farm A, for instance, belongs to the *Kqd* geological unit, which features intrusive rocks, 'Antioqueño batholith' and quartzodiorite; meanwhile, the farms B–D belongs to the *nf* geological unit featuring metamorphic rocks from central cordillera, feldspathic and Al gneiss, including migmatite and some intrusive gneiss (see Fig. 2). In other cacao-growing regions, such as Honduras, a significant correlation was found between the geology of the system, the available soil Cd and beans Cd contents (Gramlich et al. 2018). Interestingly, other studies have related the quality attributes with the farm altitude in other crops such as coffee (Morales-Ramos et al. 2020) and in cacao (Cubero et al. 1992).

As shown, the soil pollution due to Cd presence and its plant uptake risk is very harsh to assess only based on a few parameters, due to multiple factors involved in final Cd bioavailability and beans deposition. There are just a few examples of regulations for Cd in farmland soils elsewhere. For instance, according to the agricultural land soil pollution prevention law of Japan, a polluted area is designated by the Cd concentration in rice grains produced, with a threshold of 0.4 mg kg^{-1}, instead of the soil Cd concentration itself (Makino et al. 2019). Similarly, according to critical levels for Cd content in cocoa products (FAO/WHO 2018), farms producing cocoa beans with Cd contents above 0.6 mg kg^{-1}, as the case of farm A of this study, could be considered polluted by Cd. Even when the European regulation refers to transformed cocoa as powder or chocolates, there is no doubt that the permissible limit affects the international trade of dry cocoa beans, because European clients demand raw materials rather than end-products for chocolatery. In Colombia, there is still no regulation for agricultural soils nor chemical or organic fertilizers contaminated with Cd.

Predicting Cd soil fluxes in cacao farm soils

As shown in Fig. 2, due to the geological description of the municipalities of Maceo and San Roque, the most recurrent mineral found corresponds to 'Antioqueño batholith' (Restrepo-Moreno et al. 2009). Geomorphologically, the batholith is released due to continuous weathering of rock. This could be observed in the formation of hills and dendritic drainage.

The analysis of the predictive 2D-ERTs, proposes a flux or path of Cd compounds from the surface into the subsoil (Morelli et al., 2007; Jung 2008), due partially, to the percolation of agents contaminated with Cd by anthropogenic activity such as fertilizers application (Kuriakose and Prasad 2019; Satarug 2019) and due in part, to the leached organic matter on the surface by saprophytic decomposition of soil litter and fallen pods with Cd content (Meunier et al. 2003, 2004).

The 2D-ERT has an accuracy for Cd measurement of 0.03–2.76 mg kg^{-1}, which is higher in comparison with other in situ non-invasive techniques (Bravo and Benavides-Erazo 2020). The predictive ERT addresses the Cd distribution in both material vectors and direction in the two-dimensional overview (Morelli et al. 2007) of the cacao subsoil. Therefore, a mobility route could be established, which is important to further amendment applications or soil correctives. In this study, the presence of blocks or spots of Cd related to solid material was highlighted mainly in topsoil with a patchy distribution to the underground. The percolation and leaching processes mentioned above might be mediated through mechanical and biological interactions between the rhizosphere niche and the mineral composition surrounding the cacao root system.

The primary source of soil Cd is from the parent material, as the case of the igneous rock 'Antioqueño batholith' to farm A, and metamorphic rocks to farms B–D. However, as igneous rocks are reported to have Cd concentrations in the range of 0.07–0.25 mg Cd kg^{-1} and metamorphic rocks in the range of 0.11–1.00 mg Cd kg^{-1} (Traina 1999), soil Cd contents above the threshold for unpolluted soils of 0.5 mg kg^{-1} (McBride 1994) observed in the studied farms from Antioquia could be associated also to anthropogenic input, such as fertilizer application.

The use of the ERT technique, by itself, does not allow assess concentrations of materials; however, it provides the location of soil dots by which variations of electrical resistivity values are determined. This study proposes an innovative use of the 2D-ERT technique, compile with an interdisciplinary confluence, between other field techniques and laboratory tests, to be able to take advantage of the physical property of electrical resistivity in the analysis of the concentration of pollutants within the materials assessed in the subsoil (Coelho et al., 2020).

The role of fertilizers and amendments as Cd input

The Cd content in soils, soil litter and beans could be associated with agricultural practices, such as the application of foliar fertilizers. Table 5 shows the fertilization programme the farmers are using in their cocoa plantations. In farm A, for instance, it has been observed a monthly frequency and doses application of 1 L ha^{-1} of fertilizers. The application of diammonium phosphate (18–46–0) in doses of 0.080 kg $tree^{-1}$ it was noticed as especially high. In this way, the strategies to tackle Cd inputs must include the incorporation of mineral remediation and bioremediation, with an effect on the mixed addition of chelating minerals and immobilizing CdtB that in an integrative manner should diminish the bioavailable Cd, on time (Bravo et al. 2018). In addition, due to the soil litter Cd content found in farm A, the removal of litter and crop residues, which could become a highly available source of Cd when decomposing on the soil surface, should be considered as a mitigation strategy as it has been suggested in other studies (Gramlich et al. 2018; Barraza et al. 2019).

Farm B showed the highest soil Cd content in the context of the assessed farms, that could be associated with applications of a phosphate rock formulated fertilizer, potassium feldspar, ground serpentine, B, Cu, Mo, Co and Zn in doses of 0.120 kg $tree^{-1}$, twice a year, as a source of phosphorus, managing to slightly increase its content in the soil at low; however, the detectable values in the laboratory were between 10 and 14.5 mg kg^{-1} of P. In the forthcoming study, an analysis of the Cd content in fertilizers used in farms A and B is needed. However, this hypothesis is based on the fact that some phosphoric fertilizers have proved to be an important income of Cd in soils (Snoeck et al. 2016; Li et al. 2020). This could be addressed also, regarding the significant percentage of ground serpentine on its composition, which could represent a greater contribution of Cd than expected, due to the chemical and mineralogical composition of serpentine, with 'van der Waals' bounds associated with easily released Cd^{2+} ions in soil solution (Singh et al. 2020). Cd content in phosphate rocks can vary widely, depending on the origin, with contents ranging from 0.2 to 340 mg kg^{-1}, and the edaphic application of phosphate rock, or simple super phosphate, in tropical acid soils, might increase the risk of contamination with Cd in food, due to the greater availability of Cd with the concomitant soil pH dropping (Helmke 1999). There is an increasing need for cost-effective and environmentally friendly techniques to reduce metal accumulation in chocolate. According to previous studies (Trakal et al. 2011; Scaccabarozzi et al. 2020; Ondrasek et al. 2021; Rumney et al. 2021), liming using dolomitic limestone, restricted metal leaching from the soil substrate and, at the same time, in willow, alleviated plant stress imposed by toxic elements resulting in better plant growth. Moreover, a very recent paper (Liu et al. 2021) shows the benefits of dolomite phosphate rock (DPR), humic acid-activated dolomite phosphate rock (ADPR) and biochar (BC) in immobilizing Cd in subtropical soils. However, regarding the application in cocoa crops during the past years, although the application of liming material such as dolomite it has been extensively studied as an option to stabilize Cd in the soil, neutralize acidic soil and enhance metal stabilization in soil by reducing the extractable Cd concentration (Hamid et al. 2018; Ramtahal et al. 2019; Argüello et al. 2020), it has been shown that this technique needs to be reconsidered due to its efficiency in terms of time and cost for cacao in field. Furthermore, the chloride ions released from the application of KCl fertilizers, might

Table 5 The annual fertilizer programme used by farmers in the studied cacao farms

Farm	Product	Dose [kg tree^{-1}]	Frequency [year^{-1}]
A	Urea (46–0–0)	0.12	2
	Diammonium phosphate (18–46–0)	0.08	2
	Potassium chloride (0–0–60)	0.15	2
	8–5–0–6 + microelements	0.08	2
	48% B_2O_3 21% Na	0.01	2
	Dolomite lime (57% $CaCO_3$; 38% $MgCO_3$)	1	1
	Chicken manure	1	1
	Complete foliar fertilizer	1*	12
B	Urea (46–0–0)	0.06	2
	Phosphate rock, potassium feldspar, ground serpentine, B, Zn, Cu, Mo and Co	0.12	2
	Potassium chloride (0–0–60)	0.12	2
	Dolomite lime	4400	1
	Foliar fertilizer (diluted fertilizers in 200 L of water)	200*	3
	$Na_2B_4O_7 \cdot 10H_2O$ (0.8 kg ha-)		
	Magnesium sulphate (0.8 kg ha^{-})		
	Potassium sulphate (0.8 kg ha^{-})		
	Zn (0.8 kg ha^{-})		
	Si (4 kg ha^{-})		
C	Worm compound		
	Compound lime	0.7	1
D	Drench (diluted fertilizers in 200 L of water):	200*	1
	Potassium chloride (0–0-60) (20 kg)		
	Diammonium phosphate (18–46–0) (5 kg)		
	21–0–0 + 11 (CaO) + 7.5 (MgO) (7 kg)		
	H_3BO_3 (1.5 kg)		
	Zn (0.5 kg)		
	Potassium sulphate (2 kg)		
	Magnesium sulphate (1 kg)		
	Bovine manure (7 kg)		
	Horse manure (7 kg)		
	Gypsum	0.5	
	12–24–24	0.3	2

*Fertiliser dose expressed in L ha^{-1}

form Cd-Cl soluble compounds, increasing Cd bioavailability (Nino-Savala 2019), which could be the case in farms A, B and D, where the application of KCl is regularly used.

In China, for instance, Cd content in the most widely used phosphoric rock fertilizers is in the range of 0–27.2 mg kg^{-1}, with an average Cd content of 0.75 mg kg^{-1}, being diammonium phosphate (DAP) and monoammonium phosphate (MAP) the sources of 83.31% of the Cd input to the agricultural soils (Li et al. 2020). In rice-producing areas, it was found that phosphate rock fertilizers and organic fertilizers could cause Cd contamination in the soils in the order of 0.04–2 g ha^{-1} year^{-1} and 0–10 g ha^{-1} year^{-1}, respectively (Zhao et al. 2015; Wang et al. 2019). In Brazil, the Cd content in the most used phosphoric rock fertilizers is in the range of 0.40–40.03 mg kg^{-1}, with an average of 9.39 mg kg^{-1}, exhibiting the highest concentrations of Cd in phosphate rock; hence, the higher annual contributions to the soil are generated by simple superphosphate and MAP application, due to the volumes used, that can reach values up to 6.6 ± 1.1 and 4.8 ± 2.0 g Cd ha^{-1} year^{-1}, respectively (Vieira da Silva et al. 2017). Likewise, a new concern in cacao beans Pb content is emerging in this country (Ferreira de Oliveira et al. 2021).

In this study, urea (CON_2H_4) was applied to farms A and B, which is an important source of nitrogen. In previous studies in a pot experiment (Zaccheo et al. 2006), it was found that the applications of N in the form of NH_4 caused the pH dropping in the rhizosphere and significantly reached the accumulation of Cd in sunflower plants compared to nitrogen applications in the form of nitrate (NO_3). Thus, our data from the Magdalena basin region farms in Antioquia suggest that both phosphate and nitrogen fertilizers could be a triggering factor in Cd bioavailability to cacao-growing farms.

Conclusion

This study has shown that key factors, such as altitude and soil interchangeable acidity, are the best predicting variables for bean Cd content in the assessed cacao-producing farms from Antioquia. The 2D-ERT technique proved to be useful in predicting the possible path and Cd convergence from topsoil to subsoil due to both geogenic and anthropogenic Cd inputs. It was highlighted that fertilizer applications and decomposition of soil litter might have an impact on Cd dynamics through the assessed cacao systems in Antioquia. As mentioned before, the complexity of Cd dynamics in cacao systems should imply the assessment of biota and weather conditions, which have an important effect on Cd rations due to their buffer capacity in cacao-growing soils. Thus, further studies will imply the use of several factors, including those here assessed to understand Cd bioavailability and final beans deposition. The multi-approach overview will increase the opportunity to install fitted strategies adapted to each farming scenario. As bean Cd content was not correlated to soil Cd in cacao farms from Antioquia, future research is necessary to study the roll of the biota, microelements soil content and fertilizers Cd content in soil Cd bioavailability, as the effects of soil physical properties and oxygen flow through the root zone on the Cd uptake ability of cacao trees. The predictive power of the 2D-ERT technique to describe the soil Cd distribution could be improved by including topographic data and detailed soil profile descriptions in future studies.

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Data Availability The datasets used and/or analysed during this study are available from the corresponding author on reasonable request.

Declarations

Conflict interests The authors declare no conflict of interest either between the institutions implied in data acquisition or in data analysis. There is no competing interest with research, authorship or publication of this manuscript.

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