

Heavy metal fractionation in Fluvic Entisols under saline conditions in Northeastern Brazil¹

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ABSTRACT - The long-term use of agrichemicals might add some heavy metals to soils and, there is little information about the dynamics of these elements in soils under saline conditions in semiarid regions. This study aimed to investigate the dynamics of heavy metals in the different fractions of Fluvic Entisols with saline conditions under long term of coconut cultivation in a semiarid region. Composite soil samples were collected in five agricultural areas and three areas under native vegetation. Physical, chemical, and heavy metal analyses were carried out in soil (semi total and fractionated contents). Quality of irrigation water and drainage water was also evaluated. Analytical results were normalized and subjected to analysis of variance, and means were compared by Scott-Knott test ($P < 0.05$). Pearson correlation analysis was also used to assure a minimum correlation of variables justifying its use in the matrix of a factorial analysis. Semi-total contents of Cr, Ni, Pb and Zn (except Cu in some areas) were lower than previous local assessment and national guiding values, indicating that they do not cause harmful alterations in soil quality. Analyses of waters showed high levels of HCO_3^- , indicating moderate restriction to use (due to the high levels of EC, SAR, Na and Cl). Fractionation of heavy metals revealed low risk of environmental pollution since most metal contents were bound to the oxidic, organic and residual fractions. The water used in irrigation contributes to the contents of heavy metals and to the salinity condition of the evaluated soils.

Key words: Speciation. Trace elements. Salinity. Soil quality. Semiarid Brazil.

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INTRODUCTION

The increase in environmental impacts due to uncontrolled exploitation of natural resources has stimulated scientific studies seeking solutions for sustainable development. Hence, studies on the quality of soils and waters in agricultural systems need to be prioritized, since these environments may contain toxic elements such as heavy metals, which are potentially toxic to plants, animals, and human health.

Heavy metals in soil can originate from a wide range of sources, including weathered parent materials, effects of mining, traffic emissions, products of smelting, application of chemical fertilizers, and other industrial, agricultural, and business activities (JIN *et al.*, 2019). They can be present in different chemical fractions, including non-residual and residual fractions, however, the non-residual fractions (water soluble, exchangeable, organic, Fe-Mn oxide and carbonate), may potentially affect their toxicity, mobility, and bioavailability (LIU *et al.*, 2022). The toxicity of metals depends not only on their total concentration but also on their mobility therefore, it is important to understand their association with the solid phase, since they are governed by a series of physical-chemical processes, among them, soil salinity.

The irrigated perimeter of Curu-Pentecoste (PICP), an important agricultural area in the Northeastern of Brazil, due to its contribution to the economic development of the region, is almost entirely over alluvial deposits belonging to the Curu River and its tributaries, originated from river deposits, usually in unconsolidated layers of sand, clay, silty-clay, quartz, gravel, and organic deposits (COMPANHIA DE PESQUISA DE RECURSOS MINERAIS, 1998). In general, they have good natural fertility, but since early 1990s, salinity problems have been identified in more than 20% of the area (INSTITUTO INTERAMERICANO DE COOPERAÇÃO PARA A AGRICULTURA, 2010).

Some studies report that soil salinity might be the controlling factor influencing concentrations and environmental risks of arsenic (As) and other heavy metals in degraded coastal wetlands (BAI *et al.*, 2019). Since heavy metals accumulate in different soil fractionations, showing different levels of potential toxicity, bioavailability, and mobility (ZHANG *et al.*, 2015), results of fractionation analysis have been useful to obtain information on the origin, form of occurrence, bioavailability, potential mobility, and transport of elements (ACKAY; OGUZ; KARAPIRE, 2003; LIU *et al.*, 2021), allowing to identify possible environmental risks associated with the availability of heavy metals, in areas with or without anthropic influence.

Studies about heavy metals, such as bioavailability and fractionations of heavy metals in naturally contaminated soils treated with different amendments (NEJAD *et al.*, 2021); the levels of natural metals in soils (LEAL *et al.*, 2020); heavy metals and microbial community in irrigated areas (ANJOS *et al.*, 2018) have been carried out; however, the dynamics of heavy metals in soils under saline conditions in semiarid regions remain poorly documented.

Considering this knowledge gap, our study explored the following questions: 1) how is the behavior of heavy metals in the different chemical fractions of saline soils from a semiarid region? 2) is there any influence from agricultural management, parent material, or soil physical or chemical properties on the mobility and availability of heavy metals in soils under such conditions? and 3) is the dynamics of heavy metals in the soil influenced by irrigation water quality? The objective of this work was thus to investigate the dynamics of heavy metals in the different fractions of Fluvic Entisols with saline conditions under long term of coconut cultivation in a semiarid region in Brazil.

MATERIAL AND METHODS

Site location and description of soils

The study area is located within the irrigated perimeter of Curu-Pentecoste (PICP), State of Ceará, Brazil. This area contributes to the socio-economic development of Brazilian northeast (NE), due to the production of grains, pastures, sugar cane, and fruits, especially coconut (*Cocos nucifera* L.), given its adaptation to the soil and climate conditions. The area is characterized as semiarid with irregular precipitation (concentrated from February to May) with mean annual rainfall and temperature of 801 mm and 27.1 °C, respectively (EMBRAPA, 2001); classified as BSw'h' according to Köppen's classification. In the Irrigated Perimeter, water is supplied by the public dams General Sampaio, with storage capacity of 322,2 hm³ and Pereira de Miranda, with capacity for 395,6 hm³ and groundwater, however, due to the long drought period – more than 10 years, considered as the worst in the last 50 years affecting not only Ceará but most NE states in Brazil, intense soil use with furrow irrigation to meet crops water requirement and high evaporation rate, the Perimeter is less than 10% of its capacity. Besides that, according to Gheyi (2000) about 25% of irrigated areas in the NE are degraded by salinization mainly due to improper irrigation management and to climatic and environmental conditions of the region.

Sampling and analyses

Were selected five areas with low relief cultivated with coconut (*Cocos nucifera* L.) and with history of pesticides use and furrow irrigation (7-day irrigation interval) in the PICP, and three areas of native vegetation close to the cultivated areas, to serve as reference of steady-state conditions (Figure 1). The soils were classified as Neossolo flúvico (Brazilian soil taxonomy, equivalent to Fluvic Entisols, soil taxonomy), with a typical sandy loam texture. The parent material of soils in the PICP are characterized by tertiary sediments and quaternary deposits that originated the current class of soils, derived also from rocks of the crystalline basement (represented by gneisses and other minerals) associated with rocks of predominantly granitic composition and even with sedimentary rocks, such as clay-sandy sediments (CEARÁ, 2009). The description, and management history of the areas are shown in Table 1.

In each area, three composite soil samples, obtained from three random subsamples, were collected using a stainless-steel Dutch auger, at two depths, which were established to evaluate the influence of anthropic activities (0-20 cm) and parent material (60-80 cm), respectively.

Samples were air-dried, ground, and passed through a 2-mm mesh nylon sieve, to obtain air-dried fine soil. The chemical characterization followed the methodologies described by Teixeira *et al.* (2017): pH was determined in water (1: 2.5); total P extracted with Mehlich-1 solution and determined spectrophotometrically; exchangeable bases (Ca^{2+} , Mg^{2+} , K^+ , and Na^+) extracted with ammonium acetate solution pH 7.0, determined by flame photometry (K^+ and Na^+) and atomic absorption (Ca^{2+} and Mg^{2+}); and organic carbon was determined by the Walkley-Black method (GESSESSE; KHAMZINA, 2018). Irrigation water samples were also collected from the irrigation channels and in the water drained from the evaluated agricultural areas. After collection, samples were placed in hermetically closed plastic bottles and reserved for further analysis. Water samples were characterized based on the norms of the Standard Methods for Examination of Water and Wastewater (AMERICAN PUBLIC HEALTH ASSOCIATION, 2012), for the determination of pH, electrical conductivity (EC), and contents of Ca, Mg, Na, K and P. All soil and water analyses were carried out in triplicates.

Figure 1 - Location of the study area at the irrigated perimeter Curu-Pentecoste (PICP), northeastern Brazil

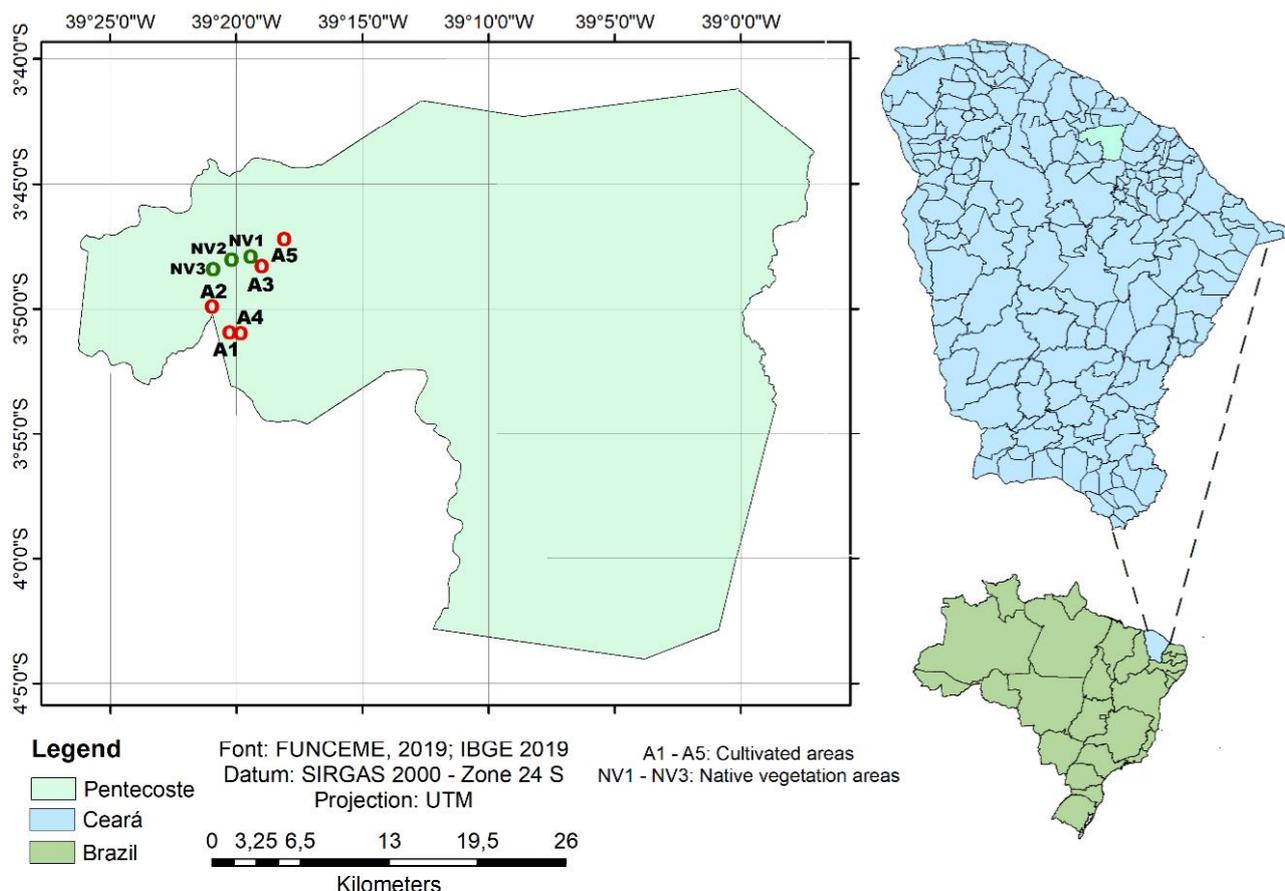


Table 1 - Description and management history of studied areas at the irrigated perimeter Curu-Pentecoste (PICP), northeastern, Brazil

Area (geographic coordinates)	Use and management history
A1 (3°51'5.27"S and 39°20'27.68"O)	Total area of 1.20 ha, located at 50 m.a.s.l., under coconut for 22 years; before that, the area was cropped to maize and beans for 16 years. Fertilization consists of cattle manure (6.25 t ha ⁻¹) and chemical fertilization-NPK (62.5 kg ha ⁻¹). Pests, diseases and weeds are controlled through the application of a variety of chemicals: monocrotophos (1.5 mL L ⁻¹), methyl parathion (1.0 mL L ⁻¹), carbosulfan (1.5 mL L ⁻¹).
A2 (3°50'7.24"S and 39°21'13.32"O)	Total area of 0.5 ha, located at 50 m.a.s.l., under coconut for 7 years; before that, the area was cropped to maize and beans for ~7 years. Fertilization consists of cattle manure (3.9 t ha ⁻¹) and 54.7 kg ha ⁻¹ of NPK. Pests, diseases and weeds are controlled through the application of a variety of chemicals: deltamethrin (0.75 mL L ⁻¹), methyl parathion (1.0 mL L ⁻¹), abamectin (1.5 mL L ⁻¹).
A3 (3°48'17.47"S and 39°19'58.45"O)	Total area of 0.65 ha, located at 51 m.a.s.l, under coconut for 7 years; before that, the area was cropped to guava for 5 years. Fertilization consists of cattle manure 3.12 t ha ⁻¹ and 20.8 kg ha ⁻¹ of NPK. Pests, diseases and weeds are controlled through the application of carbosulfan (2.0 mL L ⁻¹).
A4 (3°51'5.27"S and 39°20'27.68"O)	Total area of 1.2 ha, located at 45 m.a.s.l, under coconut for 20 years; before that, the area was cropped to maize and beans for ~10 years. Fertilization consists of cattle manure 7.8 t ha ⁻¹ and 54.7 kg ha ⁻¹ of NPK. Pests, diseases and weeds are controlled through the application of a mixture of monocrotophos (2.5 mL L ⁻¹) and carbosulfan (2.5 mL L ⁻¹).
A5 (3°47'31.98"S and 39°18'13.57"O)	Total area of 0.5 ha, located at 45 m.a.s.l., under coconut for 12 years; before that, the area was cropped to maize, beans, pepper and banana for 18 years. Fertilization consists of 55.0 kg ha ⁻¹ de NPK. Pests, diseases and weeds are controlled through the application of a mixture of monocrotophos (3.0 mL L ⁻¹) and carbosulfan (3.0 mL L ⁻¹).
NV1 (3°48'41.42"S and 39°19'57.01"O)	Area with no anthropogenic activity, located at 59 m.a.s.l.
NV2 (3°48'42.99"S and 39°20'35.56"O)	Area with no anthropogenic activity, located at 76 m.a.s.l.
NV3 (3°49'58.36"S and 39°21'17.33"O)	Area with no anthropogenic activity, located at 65 m.a.s.l.

A1-A5: Cultivated areas; NV1-NV3: Native vegetation areas.

Aliquots of soil samples were macerated in an agate mortar and sieved through a 0.3 mm mesh stainless-steel sieve (ABNT n° 50) to avoid contamination, for heavy metals analysis. Digestion was carried out in the soil samples (0.5 g of pulverized samples) from the evaluated areas (cultivated and native areas), and in reference samples certified by the NIST (NIST SRM 2709 San Joaquin Soil), to extract the semi total contents (ST) of As, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, according to the method 3051A (UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, 1998). Metals were determined by inductively coupled plasma optical emission spectrometry (ICP-OES), using the Thermo Scientific iCAP 6300 DUO. Soil heavy metals were fractionated using the methodology proposed by Tessier, Campbell and Bisson (1979), extracting the elements bound to the exchangeable (F1), carbonate (F2), oxidic (F3), organic (F4) and residual (Res) fractions.

Analytical results were normalized and subjected to analysis of variance, and means were compared by the Scott-Knott test ($P < 0.05$) using the program Assistat 7.7.

The parameters used in the chemical characterization and in the contents of the evaluated heavy metals were used as variables for the Pearson's correlation analysis ($P < 0.05$), as well as in the data matrix of the Factorial Analysis. This multivariate analysis allowed transforming the original variables (observed) into a reduced set of factors, enabling better interpretation of the data. Factors with eigenvalues higher than 1.0 were extracted by principal components analysis, and the factorial axes were rotated by the Varimax method. The database was built using the software program Microsoft Excel® (2013), whereas statistical analyses were carried out in the program Statistica 7.0.

RESULTS AND DISCUSSION

The soils were alkaline ($\text{pH} > 7.5$), except the A3 and all NV areas. The EC values in the cultivated areas were higher at the upper layer varying from 0.48 to 1.04 dS m^{-1} , whereas for native vegetation areas were higher at the deepest layers, varying from 0.35 to 0.80 dS m^{-1} . The A3 has the highest content of sand

in comparison to other cultivated areas, resulting in a medium to low cation exchange capacity (Table 2).

The recovery of elements in the certified sample (NIST SRM 2709 San Joaquin soil) varied from 70.28 to 137.72% and is within the range recommended for all evaluated elements, guaranteeing achievement in the metal extraction (NATIONAL INSTITUTE OF STANDARDS TECHNOLOGY, 2010) (Table 3).

Table 2 - Chemical and physical characterization of soils in the Curu-Pentecoste Irrigated Perimeter, Brazil ($n = 3$, STDV values in parentheses)

Characteristics	Depth (cm)	A1	A2	A3	A4	A5	NV1	NV2	NV3
pH	0 – 20	7.73 (0.18)	7.91 (0.06)	6.69 (0.44)	7.54 (0.48)	7.63 (0.31)	6.27 (0.13)	5.03 (0.16)	5.94 (0.04)
	60 – 80	7.69 (0.33)	7.6 (0.26)	7.02 (0.53)	7.8 (0.17)	7.09 (0.38)	6.16 (0.02)	6.04 (0.05)	6.58 (0.07)
Na ($\text{cmol}_c \text{ dm}^{-3}$)	0 – 20	0.66 (0.26)	1.87 (0.46)	0.45 (0.31)	1.86 (0.22)	0.71 (0.23)	0.11 (0.01)	0.14 (0.04)	0.09 (0.00)
	60 – 80	0.49 (0.24)	4.51 (0.50)	0.26 (0.02)	2.4 (0.40)	0.56 (0.21)	0.4 (0.03)	1.35 (0.17)	1.63 (1.24)
K ($\text{cmol}_c \text{ dm}^{-3}$)	0 – 20	0.18 (0.03)	0.30 (0.02)	0.26 (0.18)	0.21 (0.05)	0.23 (0.06)	0.25 (0.02)	0.13 (0.01)	0.10 (0.01)
	60 – 80	0.10 (0.05)	0.27 (0.24)	0.12 (0.01)	0.13 (0.06)	0.25 (0.06)	0.42 (0.01)	0.24 (0.01)	0.29 (0.01)
Ca ($\text{cmol}_c \text{ dm}^{-3}$)	0 – 20	2.8 (0.72)	6.06 (2.51)	0.52 (0.31)	4.33 (0.62)	3.67 (0.60)	3.92 (0.57)	0.12 (0.01)	0.66 (0.18)
	60 – 80	1.64 (0.90)	5.92 (2.80)	0.15 (0.04)	3.76 (1.96)	4.5 (0.90)	3.28 (2.11)	0.55 (0.05)	1.6 (0.25)
Mg ($\text{cmol}_c \text{ dm}^{-3}$)	0 – 20	8.55 (3.79)	7.64 (3.14)	0.68 (0.52)	4.57 (0.79)	4.22 (0.33)	4.56 (0.50)	0.29 (0.07)	0.59 (0.12)
	60 – 80	9.11 (4.35)	9.02 (2.13)	0.47 (0.08)	3.48 (1.80)	4.31 (0.70)	9.69 (0.65)	2.47 (0.16)	5.91 (0.80)
H + Al ($\text{cmol}_c \text{ dm}^{-3}$)	0 – 20	0 (0.00)	0 (0.00)	0.63 (0.55)	0 (0.00)	0 (0.00)	1.57 (0.55)	1.9 (0.17)	1.03 (0.21)
	60 – 80	0 (0.00)	0 (0.00)	0.53 (0.47)	0 (0.00)	0.33 (0.58)	1.3 (0.10)	1.27 (0.15)	0.5 (0.20)
Al ($\text{cmol}_c \text{ dm}^{-3}$)	0 – 20	0 (0.00)	0 (0.00)	0 (0.00)	0 (0.00)	0 (0.00)	0 (0.00)	0.33 (0.12)	0 (0.00)
	60 – 80	0 (0.00)	0 (0.00)	0 (0.00)	0 (0.00)	0 (0.00)	0 (0.00)	0 (0.00)	0 (0.00)
Organic carbon (OC) (g kg^{-1})	0 – 20	9.92 (1.95)	15.47 (3.38)	9.56 (1.61)	8.36 (0.44)	8.75 (1.40)	8.26 (0.52)	7.72 (2.34)	7.49 (1.15)
	60 – 80	3.66 (1.36)	5.8 (1.67)	1.82 (0.24)	3.23 (1.17)	5.35 (1.07)	3.27 (0.18)	4.06 (0.63)	3.64 (1.98)

Continuation Table 2

P (mg dm ⁻³)	0 – 20	39.21 (5.37)	15.82 (1.44)	6.53 (2.30)	25.91 (1.42)	44.34 (3.80)	5.98 (1.26)	3.15 (0.29)	11.95 (1.74)
	60 – 80	40.09 (6.94)	9.68 (0.70)	4.69 (1.93)	37.48 (7.17)	42 (5.84)	1.97 (0.22)	1.84 (0.91)	10.69 (4.68)
CECT (cmol _c dm ⁻³)	0 – 20	12.2 (3.31)	15.86 (5.66)	2.55 (0.49)	10.96 (1.61)	8.82 (1.01)	10.41 (0.85)	2.59 (0.16)	2.46 (0.38)
	60 – 80	11.34 (3.98)	19.72 (4.96)	1.53 (0.46)	9.78 (3.76)	9.95 (2.14)	14.85 (1.94)	5.69 (0.26)	9.73 (0.84)
EC (dS m ⁻¹)	0 – 20	0.61 (0.27)	0.82 (0.36)	0.48 (0.32)	1.04 (0.52)	0.93 (0.21)	0.19 (0.03)	0.2 (0.03)	0.1 (0.01)
	60 – 80	0.45 (0.24)	0.68 (0.36)	0.26 (0.01)	0.89 (0.54)	0.44 (0.19)	0.35 (0.01)	0.8 (0.11)	0.54 (0.04)
Sand (g kg ⁻¹)	0 – 20	619.83 (83.06)	434.66 (153.16)	835 (16.09)	389.16 (97.16)	429 (85.75)	595.53 (22.58)	854 (18.17)	844.2 (16.24)
	60 – 80	757.66 (141.28)	397.66 (363.24)	858.33 (5.48)	459.33 (283.70)	348.16 (127.04)	442.5 (14.24)	722.36 (15.91)	734.53 (20.47)
Silt (g kg ⁻¹)	0 – 20	319.3 (65.32)	418.26 (119.26)	135.53 (7.77)	538.56 (96.43)	499.13 (79.53)	276.9 (41.15)	97.7 (12.48)	110.9 (16.12)
	60 – 80	194.8 (125.95)	409.6 (242.92)	83.53 (21.79)	460.93 (243.07)	543.9 (109.92)	324.23 (65.43)	44.56 (3.56)	125.76 (9.84)
Clay (g kg ⁻¹)	0 – 20	60.86 (17.82)	147.06 (34.02)	29.46 (13.15)	72.26 (22.15)	71.86 (8.62)	127.56 (39.84)	48.3 (6.32)	44.9 (1.23)
	60 – 80	47.53 (19.06)	192.73 (121.58)	58.13 (27.26)	79.73 (40.80)	107.93 (20.20)	233.26 (75.17)	233.06 (19.33)	139.7 (15.64)

Where: A1-A5: Cropped areas; NV1-NV3: Native vegetation areas; STDV: standard deviation; CEC_p: Total cation exchange capacity; EC: Electrical conductivity

Table 3 - Recovery of heavy metals in the reference soil (NIST SRM 2709 San Joaquin soil) based on the USEPA method 3051a (n= 3)

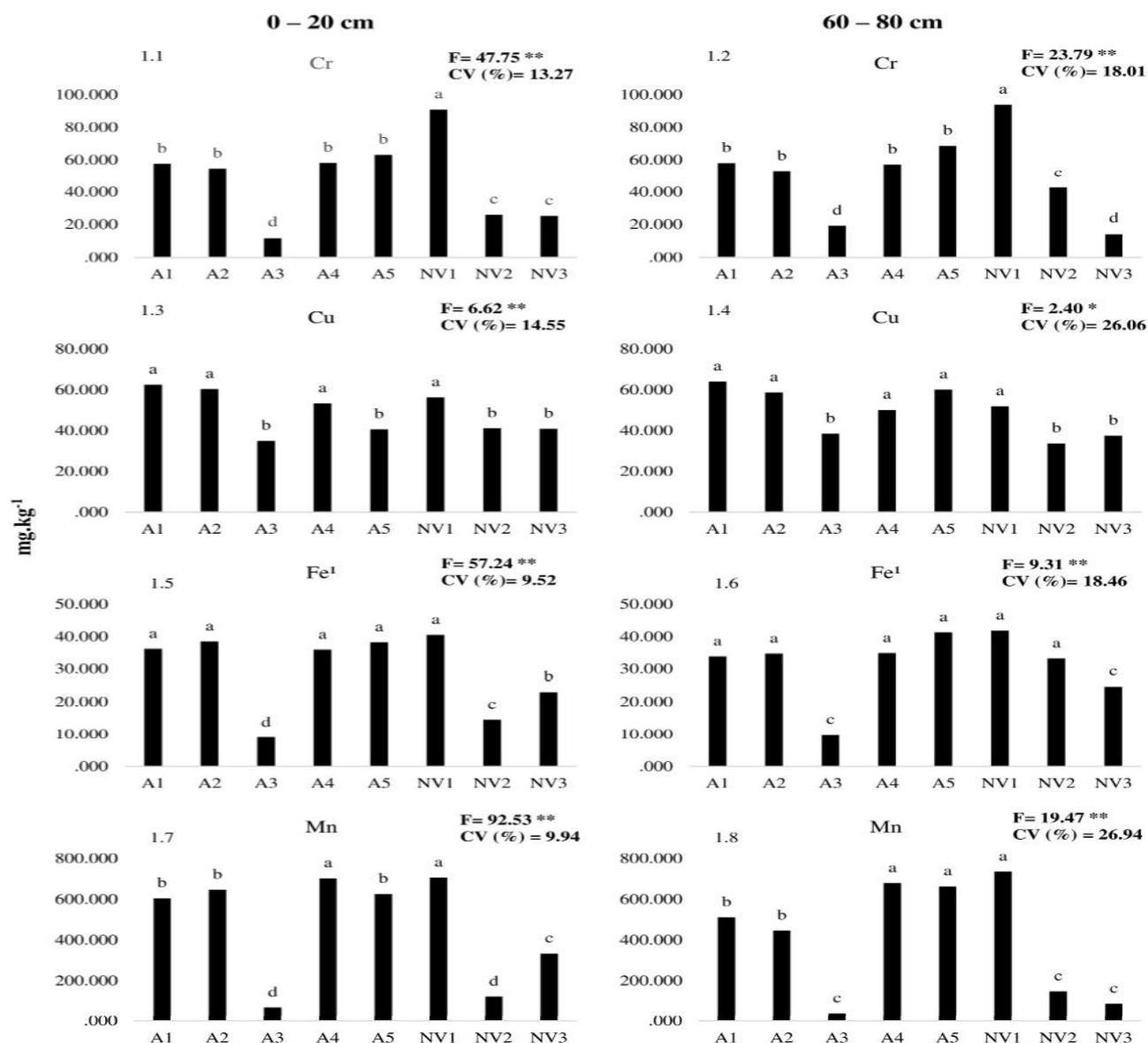
Metal	CV (NIST)	MCV (NIST)	Determined value	STDV	Recovery (R) (%)
	----- mg.kg ⁻¹ -----				
As	6.4 – 10	8.2	7.09	0.08	86.46
Cr	46 - 67	56.5	56.47	0.39	99.95
Cu	24 – 28	26	26.73	0.08	102.81
Fe	22000 – 26000	24000	22128.19	75.77	92.20
Mn	380 – 450	415	408.37	2.13	98.40
Ni	59 – 71	65	62.9	0.18	96.77
Pb	8.1 – 10	9.05	8.69	0.15	96.02
Zn	69 – 87	78	78.7	0.09	100.90

CV – Certified value range (NIST 2709); MCV – Media of certified value (NIST 2709); STDV = Standard deviation; R = percentage of recovery value (determined value /media of certified value) x 100

Despite the successful extraction of arsenic (As) from the reference sample (Table 3), its presence was not detected in any of the evaluated areas, probably due to the poverty of the parent material on this element, predominantly developed from gneisses (CUNHA *et al.*, 2014).

Semi total contents of heavy metals in soils

The results for semi-total contents of Cr, Cu, Fe, and Mn are presented in Figure 2, being higher than the results presented by Anjos *et al.* (2018) in a survey of heavy metals in the Curu River shore of Ceará State.

Figure 2 - Semi-total values (mg kg^{-1}) of Cr, Cu, Fe, and Mn in cultivated and native vegetation areas of the Curu-Pentecoste Irrigated Perimeter, CE - Brazil

Where: A1: Area 1; A2: Area 2; A3: Area 3; A4: Area 4; A5: Area 5; NV1: Native vegetation 1, NV2: Native vegetation 2, NV3: Native vegetation 3 and CV (%): Coeficiente de variación. Different lowercase letters indicate significant differences by *Scott-knott* test ($p < 0.5$). *Significant at 5% of probability by F-test; **Significant at 1% of probability by F-test. (♣) Values in g kg^{-1} for Fe

The highest semi-total content of Cr was found in the NV1 area, at both evaluated depths (Figures 2.1 and 2.2). In general, for native vegetation areas, the results were similar to those of Biondi *et al.* (2011), who found mean contents of 25.68 mg kg^{-1} in Fluvic Entisols and 90.25 mg kg^{-1} in Litholic Entisols in Northeast Brazil, without anthropic influence, which indicates the role of the parent material on the natural contents of this metal in soils of the region. Chrysochoou *et al.* (2016) also stated that conditions like the current study favor the mobilization of Cr, with

subsequent higher concentrations. No statistical difference in Cr contents was observed between the agricultural areas, except for the A3, area that has the highest content of sand, a condition that might favor the solubility and mobility of metals in soils.

The A1 area showed Cu content higher than the values found in other states of the region, as reported by Almeida Junior *et al.* (2016) (Paraíba, 28 mg kg^{-1}), Preston *et al.* (2014) (Rio Grande do Norte, 13.7 mg kg^{-1}) and

Boechat *et al.* (2020) (Piauí, 16.6 mg kg⁻¹) at both depths. The highest contents of Cu were found in A1, A2, A4, and NV1 areas, at the 0-20 cm layer and A1, A2, A4, A5, and NV1 areas, at the 60-80 cm layer (Figures 2.3 and 2.4). The area NV3 showed lower semi total contents of Cu compared to other areas, which possibly resulted from the textural differences; as mentioned before, this area has a sandy texture, indicating smaller specific surface area and lower number of negative charges on the surface of minerals, thus exhibiting a lower adsorption of metals. The content in the area A3 was similar to those in NV2 and NV3, indicating that the metals present in A3 are probably due to natural origin. Cu can have either low mobility in the soil due to interaction with organic matter and can be immobilized by the action of humic acids (MCBRIDE, 1989), or as stated by Araujo *et al.* (2019) its mobilization can be enhanced by high molecular weight aromatic compounds.

The highest contents of Fe were found in the 0-20 cm layer of the areas A1, A2, A4, A5, and NV1, which did not differ statistically; in the 60-80 cm layer, there was also no statistical difference between the areas with higher Fe contents in A1, A2, A4, A5, NV1, and NV2 (Figures 2.5 and 2.6). Since Fe represents the commonest element on Earth, it is expected to find high levels for this metal, but it is quite higher than soils from Paraíba and Rio Grande do Norte in NE Brazil (18.7 mg kg⁻¹ and 27.6 mg kg⁻¹, respectively), except for A3 at both depths in the present study, that displays the lowest contents of Fe. It is also important to pay attention to the conditions imposed on these soils, since the evaluated agricultural areas are predominantly found in low regions on the landscape, close to the Curu River bed, and have been under periodic irrigation since the crops were planted. This situation may indicate the occurrence of alternating wetting - drying cycles, which may cause reduction of elements such as Fe and Mn, increasing their availability in the soil (KHODAVERDILOO *et al.*, 2012). The Mn contents were higher at the A4 and NV1 areas, followed by the A1, A2, and A5 areas, in the 0-20 cm layer, and in A4, A5, and NV1 for the 60-80 cm layer (Figures 2.7 and 2.8), which is possibly an indication of eventual alterations in the redox potential that lead to Mn accumulation in surface. The lowest contents found in NV2, NV3, and A3 are similar to those reported by Almeida Junior *et al.* (2016) in soils from Paraíba in Brazil, with soils formed from gneiss as the evaluated soils in this study. However, the highest Mn content, found in NV1, may indicate the contribution of the clay fraction to the Mn contents in the region.

According to Khodaverdiloo *et al.* (2012), under saturated conditions, due to the low redox potential in the soil, Fe and Mn oxides are reduced under anaerobic conditions and, consequently, heavy metals are released and redistributed among the components of the solid phase;

a situation that can be imposed by the use of irrigation, leading to alternation of wetting and drying cycles. It is important to recall that the area has a furrow irrigation system, with a 7-day irrigation interval, which can certainly lead to wetting-drying cycles during the irrigation period.

The highest Ni contents in the 0-20 cm layer were found in the NV1 area, followed by the cultivated areas A1, A2, A4, and A5. In the 60-80 cm layer, the highest contents were found in the areas A2, A5, and NV1 (Figures 3.1 and 3.2), being statistically superior to those in NV2 and NV3, at both layers. Once fertilizers are not sufficiently purified during industrial processes, they usually contain several impurities, including metals and heavy metals (GIMENO-GARCIA; ANDREU; BOLUDA, 1996), which may contain up to 300 mg kg⁻¹ of Ni (MCGRATH, 1995), considered potentially harmful to the environment (CORBI *et al.*, 2018).

In addition, Ni content may be related to other factors, such as parent material, since the predominance of Ni in the residual fraction, as reported in the fractionation analysis, indicates that most of this metal may be indeed natural in the soils of the region. Additionally, its high content in NV1 should be considered as a natural indicator of this element and may possibly result from the more clayey texture of the soil in this area.

Semi-total contents of Pb are considered low varying from 10.24 to 16.52 mg kg⁻¹ in the 0-20 cm layer and from 10.33 to 14.90 mg kg⁻¹ in the 60-80 cm layer in the cultivated areas, while in native areas these values varied between 8.52 and 13.72 mg kg⁻¹ in the surface layer and between 9.55 to 18.59 mg kg⁻¹ in the subsurface layer (Figures 3.3 and 3.4), with highest contents in the areas A2 (0-20 cm) and NV2 (60 – 80 cm). Similar results of its distribution were found to those reported for some Brazilian States in the NE region, Rio Grande do Norte, 16.2 mg kg⁻¹ (PRESTON *et al.*, 2014) and Paraíba, 10.0 mg kg⁻¹ (ALMEIDA JUNIOR *et al.*, 2016), indicating in the current context low risk of environmental pollution by Pb in these areas.

For Zn, the highest semi total contents were found in areas with higher pH values, at both layers (A1, A2, A4, and A5) (Figures 3.5 and 3.6). These results agreed with Casagrande, Soares and Mouta (2008), who stated that there is a strong dependence between Zn adsorption and pH, regardless of soil depth, and this adsorption drastically increases with the increment in pH (FENG *et al.*, 2020). As reported in the Pearson's correlation analysis (data not shown), the Zn present in the agricultural areas may be essentially of lithogenic origin, due to its correlation with other metals. The lowest Zn contents were found in A3 and also in soils of native vegetation. This is in agreement

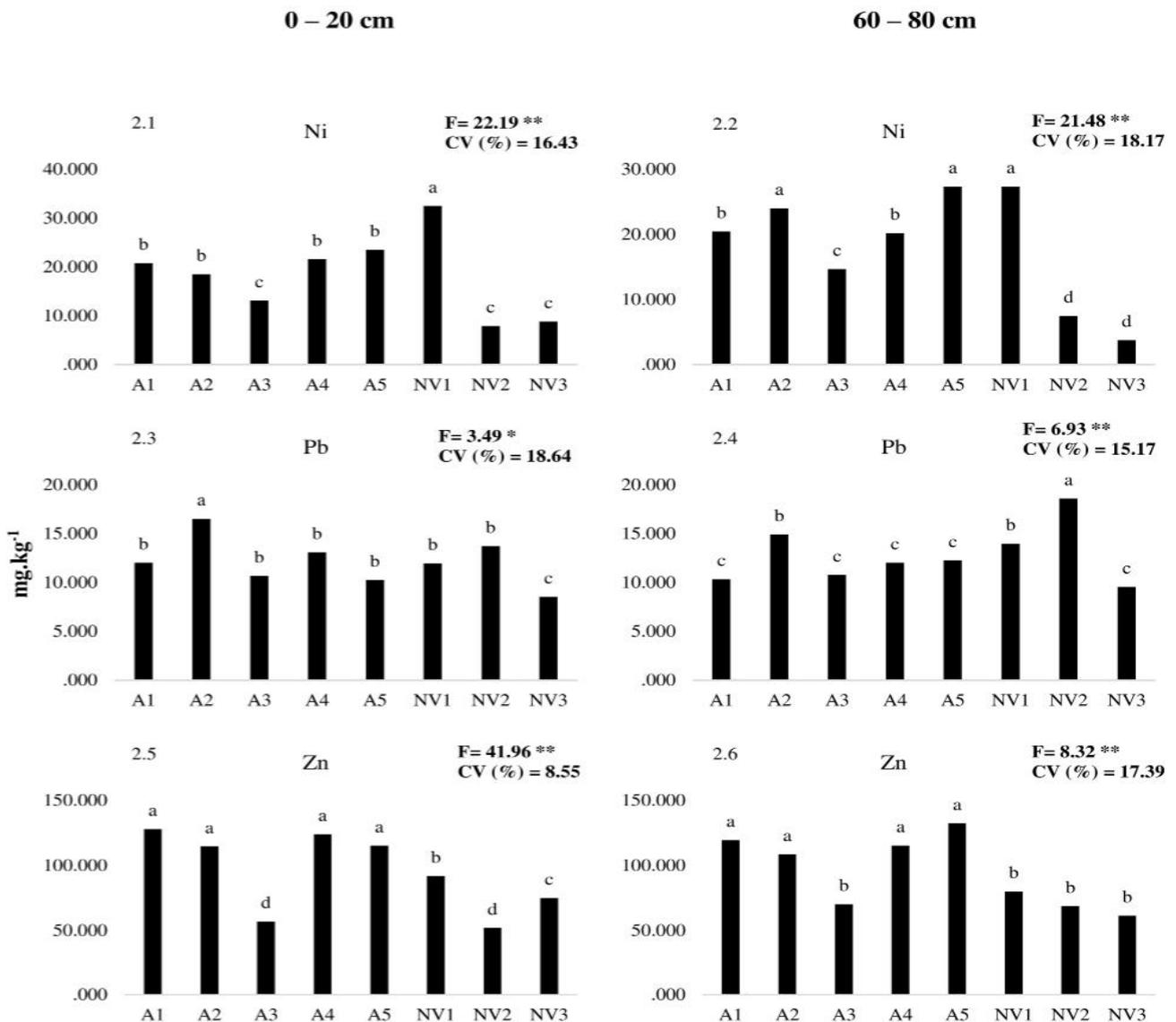
with Kabata-Pendias (2011), who stated that in soils without anthropic influence Zn contents range from 20 to 110 mg kg⁻¹, with an average of 90 mg kg⁻¹.

The lowest metals contents found in A3, are possibly due to its texture (more than 80% sand), inhibiting cation adsorption. Another factor that might influence the low content is the fact that the area has been suffering from water scarcity (precipitation and irrigation), inhibiting the solubility of metals present in the soil.

Fractionation of heavy metals

Fractionation analysis revealed higher Cr content in the residual fraction, in all evaluated areas and depths (Figures 4.1 and 4.2). These results indicate that most of this metal has low mobility and availability, possibly due to its tendency to form coordinates compounds, complexes, and chelates, promoting high stability (MCBRIDE, 1994). An increase in pH is one of the main factors favoring Cr immobilization and, in most evaluated soils, there may possibly be a strong influence of pH on Cr adsorption onto the colloid particles and formation of precipitates (MCBRIDE, 1994).

Figure 3 - Semi-total values (mg kg⁻¹) of Ni, Pb, and Zn in cultivated and native vegetation areas of the Curu-Pentecoste Irrigated Perimeter, CE – Brazil



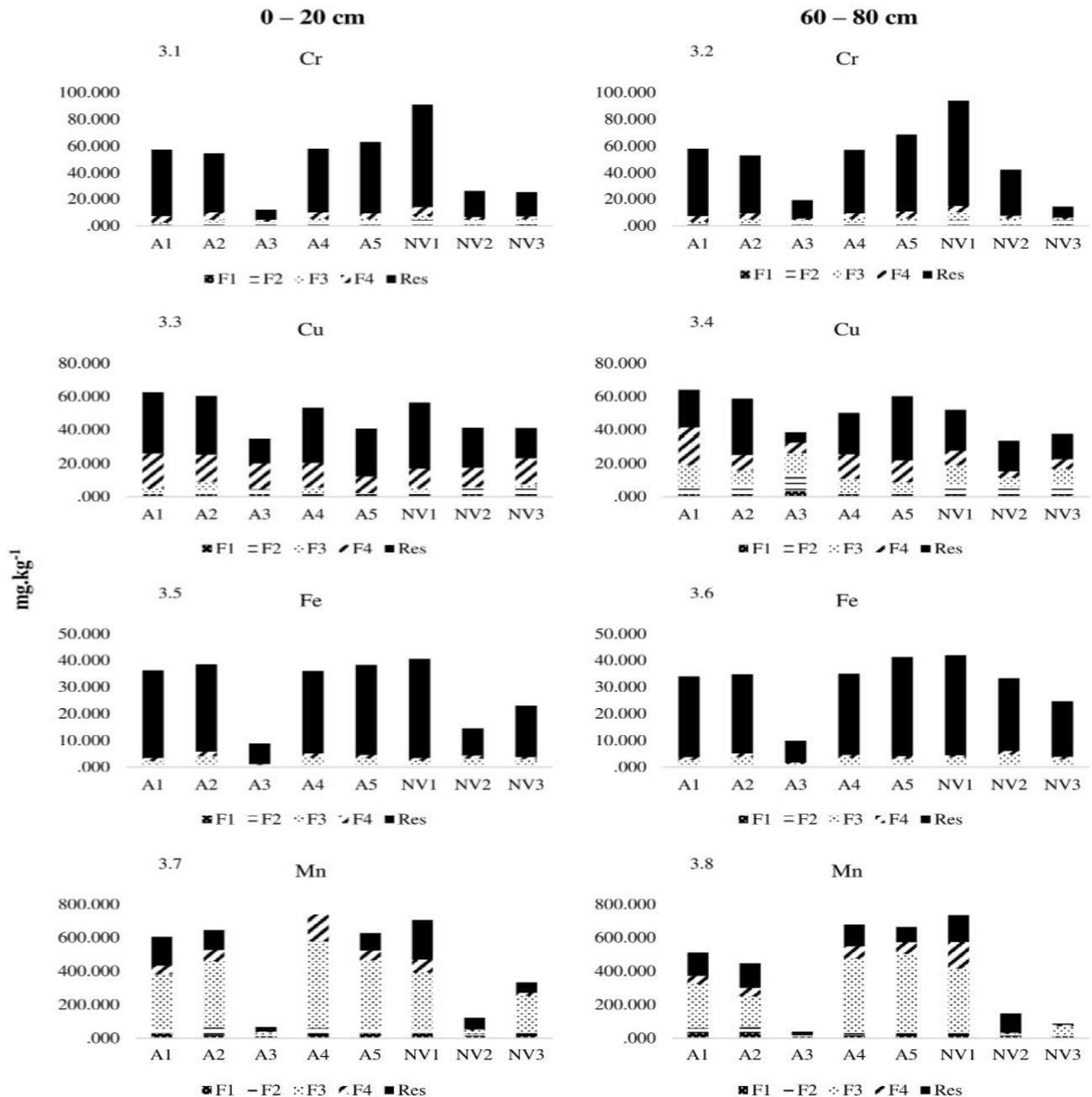
Where: A1: Area 1; A2: Area 2; A3: Area 3; A4: Area 4; A5: Area 5; NV1: Native vegetation 1, NV2: Native vegetation 2, NV3: Native vegetation 3 and CV (%): Coefficiente of variation. Different lowercase letters indicate significant differences by *Scott-knott* test (p < 0.5). *Significant at 5% of probability by F-test;**Significant at 1% of probability by F-test

The highest Cu contents (Figures 4.3 and 4.4) were found in the oxidic (F3), organic (F4) and residual (Res) fractions. In these fractions, Cu adsorption usually occurs in oxides, carboxylic, and phenolic functional groups of the organic matter and in the crystalline network of minerals, forming inner-sphere

complexes (MAHANTA; BHATTACHARYYA, 2011), which reduces its solubility. This result corroborates with Armesto *et al.* (2015), who point to these fractions as the most important in Cu adsorption.

The residual fraction (Res) showed the highest Fe content (Figures 4.5 and 4.6), much higher than those

Figure 4 - Chemical fractionation of Cr, Cu, Fe, and Mn in cultivated and native vegetation areas of the Curu-Pentecoste Irrigated Perimeter, CE – Brazil



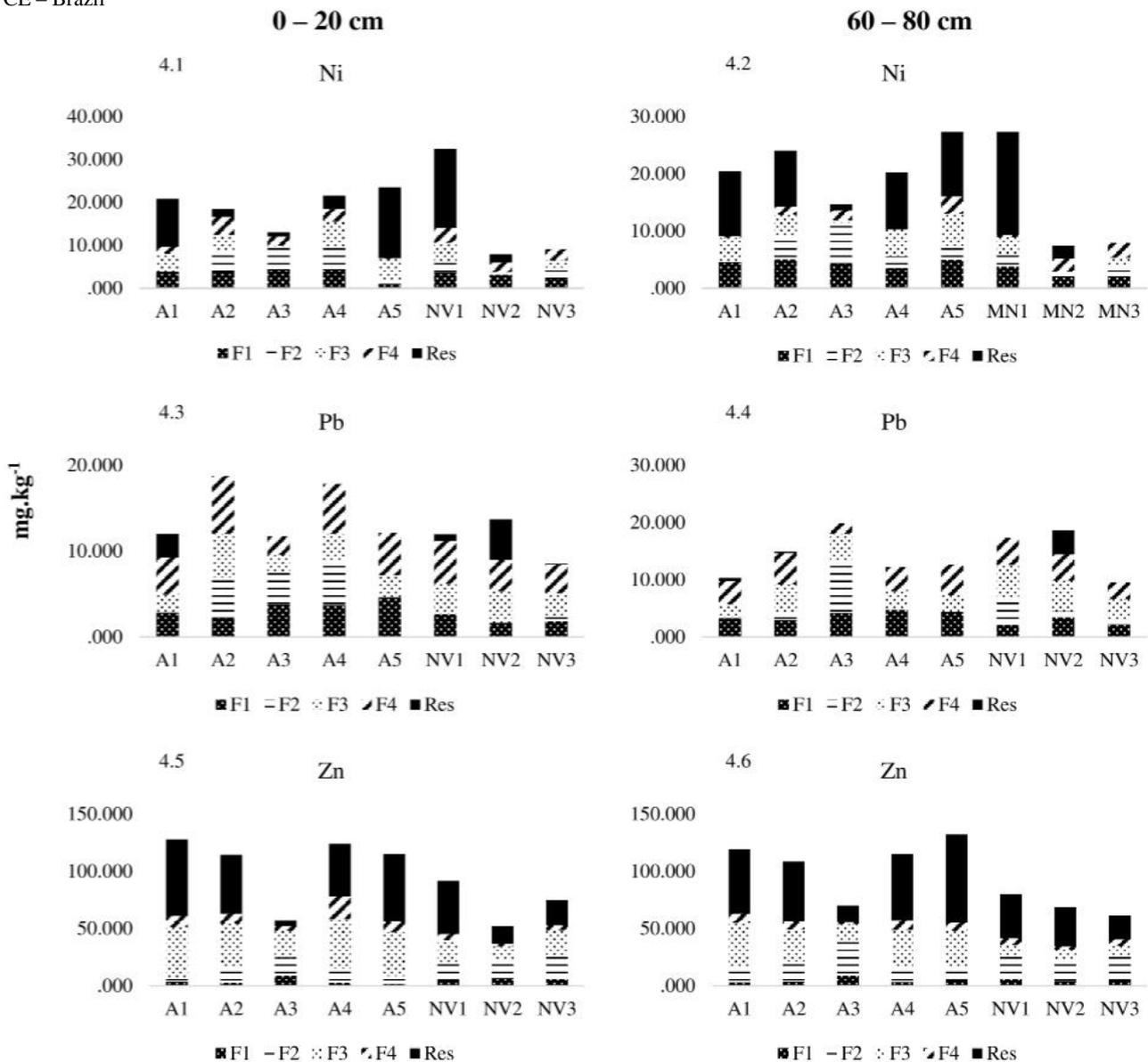
Where: A1: Area 1; A2: Area 2; A3: Area 3; A4: Area 4; A5: Area 5; NV1: Native vegetation 1, NV2: Native vegetation 2, NV3: Native vegetation 3 and CV (%): Coeficiente de variación. Different lowercase letters indicate significant differences by *Scott-knott* test ($p < 0.5$). *Significant at 5% of probability by F-test; **Significant at 1% of probability by F-test. (♣) Values in $g\ kg^{-1}$ for Fe

of the other fractions evaluated in all areas and for both layers, indicating that most of this element has low availability in the soil. Most of this metal may be present within the crystalline network of primary minerals, exhibiting reduced solubility, or even in the form of well-crystallized Fe oxides and other more resistant minerals (SILVA; VITTI, 2008). Higher pH values in the agricultural areas, compared with native areas, may, in turn, indicate adsorption of metals onto the surface of the minerals and, consequently, reduction in the availability of these elements, decreasing the solubility of metals in the soil (FENG *et al.*, 2020).

The oxidic fraction (F3) showed the highest Mn contents in the areas A1, A2, A4, A5, NV1, and NV3, at both depths (Figures 4.7 and 4.8). The predominance of Mn in the oxidic fraction can be expected since this element is also one of the natural constituents of the oxides (ALLOWAY, 2013). Significant Mn contents were also found in the organic and residual fractions of the areas A1, A4, and NV1.

The analysis of Ni fractionation (Figures 5.1 and 5.2) indicated for most areas in the surface layer, similar distribution between the fractions and low contents of this metal. In the subsurface layer, Ni is present at higher

Figure 5 - Chemical fractionation of Ni, Pb, and Zn in cultivated and native vegetation areas of the Curu-Pentecoste Irrigated Perimeter, CE – Brazil



Where: A1: Area 1; A2: Area 2; A3: Area 3; A4: Area 4; A5: Area 5; NV1: Native vegetation 1, NV2: Native vegetation 2, NV3: Native vegetation 3 F1: Exchangeable fraction, F2: Carbonate fraction, F3: Fe-Mn Oxide fraction, F4: Organic fraction, Res: Residual fraction

concentrations in the residual fraction of the areas A1, A2, A4, A5, and NV1, indicating that most of this metal is due to the genesis of the soils in the region. Although Ni was found in fractions of higher mobility, it should be considered that, under the studied conditions, this element has a low probability of causing damages to the environment, since the values are lower than other areas of similar characteristics in the NE region and without harmful report, e.g. Rio Grande do Norte with 19.8 mg kg⁻¹ (PRESTON *et al.*, 2014).

The analysis of Pb fractionation (Figures 5.3 and 5.4) also showed, among the fractions, similar distribution between the areas, which may be due to the affinity between Pb and functional groups of the organic matter and to the possibility of Pb being chemisorbed on silicate oxides and minerals, and precipitated as carbonate, hydroxides or phosphate under high pH conditions (MCBRIDE, 1994), forming low-solubility compounds.

The highest Zn contents were found in the residual (Res) and oxidic (F3) fractions, for most of the soils and depths (Figures 5.5 and 5.6), agreeing with Hadlich and Ucha (2013), who evaluated Zn availability in soils that receive organic and mineral fertilization, and observed that most of Zn is bound to these fractions. The predominance of Zn in these fractions is important from the environmental point of view because its retention may play a fundamental role in the control of the mobility of heavy metals in the environment.

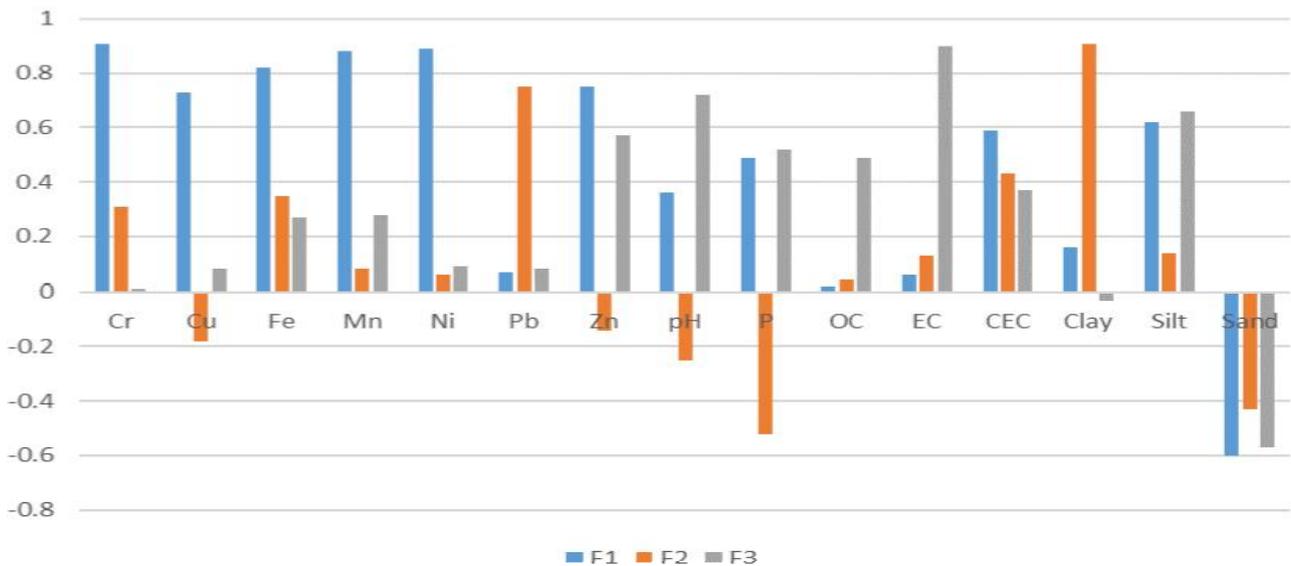
In general, the difference in the semi total contents of heavy metals between four cultivated areas (A1, A2, A4, and A5) and two native vegetation areas (NV2 and NV3), evidenced by significant differences in the analysis of variance, may indicate addition of metals in the soils of the region due to the use of agricultural inputs.

The results of Pearson’s correlation analysis (data not shown) demonstrated a significant positive correlation among metals (Cr, Cu, Fe, Mn, Ni, and Zn), and between metals and CEC, which indicates that these metals are retained onto the surface of the colloids. The correlation between metals may be due to their physical and chemical similarities, since they are transition metals and have similar atomic numbers, which may indicate that there is interaction between these elements, instead of competition. Chemically similar metals can also be found in the soil associated with the same ores and interact in the same way (CUNHA; NASCIMENTO, 2009), which may indicate that they come from the same parent material that originated this soil.

Factorial Analysis

The factorial analysis allowed to extract three factors with eigenvalues higher than 1, indicating influence of some variables. The accumulated factors explained 75.46% of the total data variance, and representative factorial loads were considered as those in which the absolute value was higher than or equal to 0.6 (Figure 6).

Figure 6 - Loadings of semi total heavy metal contents and soil properties on VARIMAX-rotated factors from cultivated and native vegetation areas from the Curu-Pentecoste Irrigated Perimeter, CE - Brazil



F: Factors, considered significant $\geq |0.60|$ Eigenvalues (7.48, 2.37, 1.47 for F1, F2 and F2, respectively); Percentage of total variance (%) (49.86, 15.77, 9.83 for F1, F2 and F3, respectively) and Cumulative percentage variance (%) (49.86, 65.63, 75.46 for F1, F2 and F3 respectively)

Factor 1 explained 49.86% of the total data variation, indicating influence mainly of Cr, Cu, Fe, Mn, Ni, Zn, silt, and sand. The high positive factorial loads in most metals may indicate association between these elements, especially in the form of Fe and Mn oxides, suggesting also high geochemical affinity. According to Cunha *et al.* (2014), the high correlation between heavy metals in the first factor indicates associated occurrence of these elements in the parent material.

In factor 2, high factorial loads were observed for Pb and the clay fraction. These results indicate, as already discussed, the adsorption of this metal onto clay minerals (MCBRIDE, 1989). Preston *et al.* (2014), in soils of Rio Grande do Norte state, Northeast Brazil, also found a high factorial load for Pb, indicating that Pb has been associated with environmental problems, suggesting anthropic influence.

High factorial loads were found for silt, EC, and pH in factor 3, which can be related to soil salinity, especially in agricultural areas. Still regarding the agricultural areas, the quality of irrigation water in these areas must be considered since depending on the water quality may favor the addition of salts such as carbonates, bicarbonates, and salts of weak inorganic acids, which may eventually increase pH and soil salinity (PIVELI, 2014).

Irrigation water analysis

It is worth mentioning that since 2012, there has been an average reduction of about 50% in the rainfall levels, compared with the historical mean for the Curu Region. According to the farmers, it substantially affected the collection of water in the A3 area.

The pH, in all areas, was slightly alkaline for both sources, being the irrigation water slightly higher than the

drained water (Table 4). Such alkalinity may be due to the presence of bicarbonates since they are one of the main components of water alkalinity (PIVELI, 2014). Hence, it is probable that irrigation water is somehow contributing to the increase in soil pH, through the addition of salts such as bicarbonate.

The EC of the water samples varied from 0.82 to 1.17 dS m⁻¹, whereas SAR ranged from 3.29 to 4.89. This range of values demonstrates, according to the classification cited by Ayers and Westcot (1999) and based on the concepts developed by the US Salinity Laboratory, that there is a moderate risk of sodification (MINHAS; QUADIR; YADAV, 2019) by the use of the irrigation water, leading to a reduction in water infiltration, due to the dispersing effect of Na in soil. These results may also indicate possible problems of salinity, thus favoring the reduction in the osmotic potential of the soil solution, reducing water availability, and accentuating the toxicity of certain ions to plants.

Still according to Ayers and Westcot (1999), these samples showed moderate degree of restriction to use for Na and Cl, requiring caution in the irrigation, since Na has harmful effects on the soil, disturbing colloidal aggregates, leading to the destruction of texture and clay-humic complex; on the other hand, Cl may cause leaf chlorosis in the crops, generating necrosis on the edges of the leaves (EMBRAPA, 2010).

All water samples, according to the irrigation water classification criteria established by Ayers and Westcot (1999), showed adequate levels of pH (6 – 8.4), Ca + Mg (< 5 mmol_c L⁻¹) and K and P levels within the common range for irrigation water (0 – 2 mg L⁻¹), but have moderate restriction to the use of irrigation in terms of HCO₃ (1.5 – 8.5 mmol_c L⁻¹) due to the potential risk of

Table 4 - Chemical characterization of irrigation water (A) and drained water (B) from the Curu-Pentecoste Irrigated Perimeter, Northeastern Brazil

Area	Source	pH	EC	K	P	Na	Cl	HCO ₃	Ca	Mg	SAR
			dS m ⁻¹	mg L ⁻¹	mmol _c L ⁻¹						
A1	A	7.95	0.82	0.33	0.00	4.51	5.90	2.48	0.67	2.05	3.87
	B	7.13	0.95	0.24	0.04	4.90	6.60	3.58	1.29	2.39	3.61
A2	A	7.76	1.09	0.57	0.04	6.17	8.60	2.86	0.90	2.78	4.55
	B	7.28	1.17	0.18	0.04	6.65	9.10	3.66	1.70	2.66	4.51
A4	A	7.71	1.09	0.14	0.03	6.52	7.70	3.96	0.87	2.69	4.89
	B	7.25	0.97	0.52	0.54	4.52	7.00	2.34	1.26	2.38	3.35
A5	A	7.92	1.07	0.15	0.09	6.17	7.30	3.67	1.01	2.59	4.59
	B	7.22	0.95	0.5	0.56	4.43	7.10	2.37	1.26	2.36	3.29

EC: Electrical conductivity. SAR: Sodium adsorption ratio

Table 5 - Heavy metal contents in irrigation water (A) and drained water (B) from the Curu-Pentecoste Irrigated Perimeter, Brazil

Area	Source	As	Cr	Cu	Mn	Pb	Zn
		mg L ⁻¹					
A1	A	0.003	0.002	0.021	ND	0.019	ND
	B	ND	0.001	0.021	0.526	0.023	ND
A2	A	0.008	0.002	0.020	ND	0.019	ND
	B	0.018	0.002	0.022	ND	0.015	ND
A4	A	ND	0.002	0.024	ND	0.012	0.249
	B	0.011	0.002	0.018	ND	0.014	ND
A5	A	0.013	0.002	0.018	ND	0.014	ND
	B	0.012	0.002	0.019	ND	0.014	ND
Conama*		0.033	0.05	0.013	0.5	0.033	0.5

ND: Not detected. * Conselho Nacional do Meio Ambiente (2005) (National guiding values)

alkalinization. For P, according to national level criteria (CONSELHO NACIONAL DO MEIO AMBIENTE, 2005), the surface waters showed concentrations within the maximum limit allowed for Type-II water bodies (0.1 mg L⁻¹), an environment characterized as lotic, i.e., with running water. For the drainage waters, the values were higher than the allowed limit in A4 and A5. In the areas A1, A4, and A5, the P concentration in the drained water was higher than that in the surface water. These results may indicate a possible transfer of P in the subsurface due to the irrigation or that the use of phosphate fertilizers and agrochemicals may be favoring the increase in P concentration in these waters.

The analysis of the contents of metals in irrigation and drain waters showed concentrations within the acceptable limits for As (< 0.033 mg L⁻¹), Cr (< 0.050 mg L⁻¹), Pb (< 0.033 mg l⁻¹), and Zn (< 5.00 mg L⁻¹). However, there were concentrations above the established limits for Cu (0.013 mg L⁻¹), in all areas, and Mn (0.50 mg L⁻¹) in the drainage water of the area A1 (Table 5), according to Brazilian standard levels (CONSELHO NACIONAL DO MEIO AMBIENTE, 2005).

It is possible that Cu has natural origin from the transport of sediments suspended in the water of the irrigation channels since the results found in both types of sources (irrigation and drained) were similar. For Mn, according to Piveli (2014), its occurrence in waters is rare, presenting itself in the oxidation states of Mn²⁺ (more soluble form) and Mn⁴⁺ (less soluble form). Thus, possible alterations in the redox potential through wetting and drying cycles caused by irrigation or even a possible rise in the water table may have led to alterations in Mn mobility and solubility in this area.

CONCLUSIONS

1. The highest contents of heavy metals are present in the residual, oxidic, and organic fractions, indicating a reduced risk of causing environmental pollution in the evaluated areas since heavy metals normally have low potential of solubility and availability in these fractions;
2. Most of the quantified metals result from the interaction of soil properties and characteristics such as pH, texture, relief, and alterations in the redox potential by wetting and drying cycles caused by irrigation (in the agricultural areas), in this case leading to availability and redistribution of heavy metals in quantifiable fractions. Also, the high contents of heavy metals in areas without anthropic influence indicate the role of parent material on the natural contents in soils of the region;
3. The water used in irrigation contributes not only to the contents of heavy metals in the evaluated areas, specifically in the case of Cu, but also to the salinity condition of soils with a potential risk of alkalization. It is recommended the water used for irrigation be monitored to guarantee its use and to avoid environmental problems such as those caused by salinity or heavy metals.

CONFLICTS OF INTERESTS

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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