#### **REVIEW**



# **Heavy metals distribution in diferent parts of cultivated and native plants and their relationship with soil content**

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#### **Abstract**

In semiarid region of Irecê, state of Bahia, Brazil, there are superfcial elongated strips in form of lateritic crust derived from hydrothermal weathering of sulfde known as "gossans" with heavy metals anomalies. Thus, this study aimed to evaluate the presence and concentration of metals As, Cd, Pb, Cu, Cr, Fe, Mn, Ni, Ti, and Zn in diferent parts of cultivated and native plants in "gossan" area and relationship with soil content, in an area that has been used for decades by small family farmers for the crops production and raising small animals. The metals were analyzed by ICP-OES in plant and soil extracts obtained after acid digestion (USEPA SW-846 3050B). As, Cd, and Ni were not found in the evaluated plants. Pb, Fe and Ti concentrated in the roots of several plants, with emphasis on bufel grass (Pb and Fe) and corn and white pinion (both Fe and Ti). Zn and Mn were distributed in all parts of plants evaluated. Cu levels found were quite below of phytotoxic levels. Signifcant positive correlation between lead in root and soil and negative between lead in stem, leaf, and soil were observed, indicating a plant protection mechanism concentrating lead in the root without translocating it to the aerial part. Similar behavior has occurred in relation to Cu, concentrating it in the root and fruit. Fortunately for the farmers and consumers, the highest concentration of heavy metals was observed in the roots of both cultivated and native plants.

**Keywords** Lead · Copper · Chromium · Iron · Manganese · Zinc

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## **Introduction**

The acquisition of macronutrients (C, H, O, N, P, K, Ca, Mg, and S) and micronutrients (Cu, Fe, Mn, Zn, Ni, B, Mo, and Cl) by plants for their growth occurs in the great majority in the soil. As a result of limited capability for the selective uptake of those essential elements by plants, they take up non-essential elements as heavy metals such as arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), Copper (Cu), iron (Fe), lead (Pb), manganese (Mn) mercury (Hg), nickel (Ni), silver (Ag), Titanium (Ti), and zinc (Zn) (Appenroth [2010;](#page-14-0) Kabata-Pendias [2011;](#page-14-1) Kirkby [2012](#page-14-2)). According to Kabata-Pendias [\(2011\)](#page-14-1), Ni, Zn, Pb, Mn, and Cu are found in plants parts in larger amounts varying according to plant species, plant parts or tissues, and the absorbed metal. It should be noted that some of those elements considered as heavy metals are essential to plant metabolism as Fe and Zn, and others as As and Pb are not, but when present in bioavailability forms and at excessive levels, they have the potential to become toxic to plants (Nagajyoti et al. [2010\)](#page-14-3).



During the last 20 years, accumulation of heavy metals in agricultural soils and cultivated plants has been the subject of a major concern in Brazil, especially for environmental safety and issues related to human nutrition and animal feed. Transfer of metals to the human food chain is possible by consuming food plants, and one of the ways to assess those contribution may be the evaluation of heavy metals concentration in plant tissues, in addition to transferences via contamination of water bodies, both superficial and subsurface (Chang et al. [1987](#page-14-4); Soares et al. [2005](#page-14-5); Silva et al. [2007](#page-14-6)).

According to the United States Environmental Protection Agency (USEPA), the toxicity level is given based on heavy metal content in soil that causes 50% of growth plant reduction. The priority list of hazardous substances published by Agency for Toxic Substances and Disease Registry (ATSDR) from United States Centers for Disease Control and Prevention (US-CDC) includes As, Pb, Hg, Cd and hexavalent Cr among the 20 most signifcant potential threat to human health due to their known or suspected toxicity and potential for human exposure at the USA (ATSDR [2019\)](#page-14-7).

In Irecê region at the north-central zone of the state of Bahia, Brazil, there are an elongated and discontinuous strips in lateritic crusts forms derived from the acting of weathering associated with hydrothermal fuids on sulfde mineralization, being the main minerals oxidized the pyrite  $(FeS<sub>2</sub>)$ , sphalerite (ZnS), and galena (PbS). The superficial portion of those strips are called "gossan" (Oliveira et al. [1993](#page-14-8)) where commonly has been detected the presence of heavy metals as anomalies.

In a characterization work of representative soils in Irecê region, Paiva ([2010\)](#page-14-9) analyzed some heavy metals in soil samples collected from four soils profles located close to each other on one of those "gossans." The results showed that Pb, Cr, and Zn total levels are within investigation range according to Brazilian Environmental Legislation and Mn high levels compared to a profle located in an area outside the "gossan" (Paiva [2010\)](#page-14-9). Given the above, an increase in the concentration of metals in plants that growth in this environment beyond the levels commonly found in plants that growth in areas with low levels of heavy metals may occur, and therefore, special attention should be given to the possibility of humans and animals being exposed to those heavy metals (Berti and Jacobs [1996\)](#page-14-10).

Sungur et al. [\(2014\)](#page-14-11) evaluated the mobility, availability, and bioavailability of metals, the relationships between the soil properties and diferent forms of metals, and the relationship between the uptake of metals by corn grain samples and the diferent forms of metals using the BCR sequential extraction method in soil samples. The wet digestion was used to determine the total concentration in corn grain and in soils samples from an Entisol (Soil Taxonomy)/Fluvisol (WRB/FAO) at the Troy National Park, Turkey. The results showed that Cd, Mn, and Pb concentrations of corn grains



were similar to the F1 fraction of soil samples, Cu concentration to the F2 fraction, and Ni and Zn to the F1 and F2 fractions of soil samples. F1 and F2 fractions are the most soluble (more available) fractions, and these results indicate that plants could uptake basically the heavy metals from these fractions and therefore insert these metals into the food chain.

Due to all the environmental concerns regarding the occurrence of heavy metals in soils, the possibility of uptake and accumulation of metals in plants with the consequent possibility of introducing these metals into the human food chain, and the previous detection of heavy metals at levels that has been considered high according to the Brazilian Environmental Legislation in studies in Irecê region, it is evident the need to evaluate the behavior of heavy metals in the soil–plant continuum in this important agricultural and livestock pole in the northeast region of Brazil. Areas around the "gossans" have been used for decades for beans, corn, castor bean and other crops production and for small animals creation. So, the main objectives of this study were determine the heavy metals in diferent parts (root, stem, leaf, and fruit) of cultivated and native plants and its relationship with these soil elements occurrence.

## **Materials and methods**

#### **Study area**

The study area is located in Municipality of Lapão, State of Bahia, Brazil, near the Tanquinho district at a medium altitude of 740 m above sea level. According to Bomfm et al. [\(1985](#page-14-12)), the studied area constitutes the main "gossan" in the region. Soils developed from it occupy small punctual strips in an area with a 13.5 km length and 0.5 km average width.

Predominant soils in the area are classifed as Oxisols and Inceptisols (Soil Survey Staff [1999](#page-14-13)) and as Latossolo Vermelho-Amarelo Eutrófico cambissólico (Ferralsol), Cambissolo Háplico Tb Eutrófco latossólico (Ferralic Cambissol), and Cambissolo Háplico Ta Eutrófco latossólico (Ferralic Cambissol) according to the Brazilian Soil Classifcation System (Santos et al. [2018\)](#page-14-14) and International Soil Classifcation System (FAO/WRB [2015](#page-14-15)). Clay content varies between 510 and 650 g kg−1, and the silt content varies from 150 to 200 g kg<sup>-1</sup> (Paiva et al. [2015](#page-14-16)). It is assumed that the heavy metals come exclusively from the parental material since all soils in the area were not managed using lime or fertilizers.

The studied area has been cultivated for over 40 years by small family farmers for bean, corn, castor bean and other crops production in addition to grazing, forage palm, and natural "caatinga" vegetation. Small animals (goats, sheep, and chickens) are also raised in the area.

#### **Soil and plant sampling**

The soil samples were taken from the surface (0–0.20 m) and subsurface (0.20–0.40 m) layers at 25 georeferenced points (Table [1](#page-2-0)), located in the "gossan" center and at 25 and 50 m in the north and south directions. Non-metallic tools were using during the sample collection, and all samples were taken to laboratory in polyethylene bags. The soil samples were air-dried at room temperature (around 25 °C) and sieved through 2.00 mm sieve (10 mesh). For heavy metals analyzes, portions of the samples were prepared by passing them through a 0.250 mm (60 mesh) with the assistance of an agate mortar to grind and homogenize the samples.

Cultivated and native plants were also randomly collected from the same 25 points where the soils samples have been sampled (Table [1](#page-2-0)). The 34 plants were collected at diferent growth stages due to the impossibility of standardization and separated into roots, stems, leaves, and fruits whenever possible. The samples were stored in paper bags and transported to the laboratory, where they were cleaned to remove surface impurities, dried to constant weight (60 °C for 72 h) in an air-circulating oven, and ground.



<span id="page-2-0"></span>**Table 1** Geographic coordi of reference points for plan soil sampling and common scientific names of the sam plants



#### **Soil and plant analysis**

The digestion of soil and plant samples was made in triplicate in a digester block, using the SW 846-3050B method (USEPA [1996](#page-14-17)), including blank tests. High-purity reagents were used in this analysis. The procedure described below was used for both plant tissue and soil samples.

Half a gram  $(0.5 \text{ g})$  of dried plants tissues or soil was placed in digestion tubes, and 5 mL of nitric acid  $(HNO<sub>3</sub>—65%, v/v)$  was adding, followed by a heating up to 95 °C for 1 h. After cooling the samples for 20 min, 1 mL of hydrogen peroxide (30%, v/v) was added and the samples were heated up to 95 °C. The addition of 1 mL of hydrogen peroxide  $(30\%, v/v)$  was repeated until the effervescence reaction decreased or the sample appearance did not change, taking care not to add more than 10 mL of hydrogen peroxide (30%, v/v) in total. This procedure was used to oxidize organic matter and releasing metals bound on this fraction. After adding the last hydrogen peroxide aliquot, the samples were cooled for 20 min, then adding 5 mL of hydrochloric acid (HCl—65%, v/v), with subsequent heating up to 95 °C. The samples were heated until the fnal volume reaches almost 5 mL. Then, the samples were cooled for about 30 min and fltered with blue band flter paper. The whole filtrate was collected in a 25 mL volumetric flask, and the volume was flled with deionized water with a conductivity of 1 μS cm−1. All laboratory materials used were previously decontaminated with soaking in  $10\%$  HNO<sub>3</sub> solution and then washed with deionized water having a conductivity of 1  $\mu$ S cm<sup>-1</sup>.

Determinations of As, Cd, Pb, Cu, Cr, Fe, Mn, Ni, Ti, and Zn were carried out by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent, 720 Axial model).

Based on the data obtained for each element and parts of the plants, and inspired by Khan's et al. [\(2016](#page-14-18)), determination of distribution coefficient was determined the heavy metal distribution coefficient in the plant of each specie by the equation:

$$
DC_i = \frac{HM_i}{HM_r + HM_s + HM_l + HM_f}
$$
 (1)

where  $DC<sub>i</sub>$  = distribution coefficient ranging from 0 up to 1;  $i = root$ , stem, leaf, and fruit;  $HM_r = root$  heavy metal (mg kg<sup>-1</sup>); HM<sub>s</sub>=stem heavy metal (mg kg<sup>-1</sup>); HM<sub>1</sub>=leaf heavy metal (mg  $kg^{-1}$ ); and HM<sub>f</sub> = fruit heavy metal  $(mg kg^{-1})$ .

In species without fruit at the sampling time, Eq.  $(1)$  $(1)$ denominator was  $H_r + H_s + H_l$ .

#### **Statistical analysis**

All data were initially evaluated for normality using Shapiro–Wilk test, followed by descriptive statistics analysis  $(average, coefficient of variation—CV, minimum, and maxi$ mum) using the computer-based Statistica software, version 7.0.

The data were standardized to verify the similarities in relation to metal distribution pattern in the plants parts into homogeneous groupings by hierarchical cluster analysis (HCA). Euclidean distance was adopted as a similarity measure and Ward's method to link the cases with each other (Sena et al. [2002\)](#page-14-19).

The data were submitted to principal component analysis (PCA) in order to assess the metals distribution in the diferent plants parts, considering only the variables that presented a factor load value above 0.60 (Hair Júnior et al. [2009](#page-14-20)). The Kaiser [\(1958\)](#page-14-21) criterion was adopted to defne the number of CPs that indicated the greatest variance explanation, that is, only components with eigenvalues > 1 and accumulated variance  $\geq$  70% were maintained in the system (Rencher [2002\)](#page-14-22).

Statistical analyzes were performed with the support of R software version 3.4.1 (R Core Team [2019\)](#page-14-23), by using the packages *cluster, purrr*, and *factoextra*.

## **Results and discussion**

Among the evaluated elements, Cu, Cr, Fe, Mn, and Zn were found in the roots, stem, leaves, and fruits when considering all plants evaluated (Table [2](#page-4-0)). The elements Pb and Ti were found in the roots, stem, and leaves, while As, Cd, and Ni were not detected in any part of any of evaluated plants. It should be noted that the identifcation of the presence of a certain element in the plant tissue is the result of the detection capability of the used method (detection limit). In addition to the detection limit, it is also important to consider that during the sample collection, only the species angico, banana, bufel grass, bean, custard apple, red mombin, and "umburaninha" had fruits.

<span id="page-3-0"></span>In all parts of the plants, the elements Fe, Mn, and Zn are always present with the highest average concentrations among the evaluated elements resulting in the following orders from the highest to the lowest concentration:  $Fe > Zn > Mn$  for root;  $Fe > Zn > Mn$  for the stem;  $Fe > Mn > Zn$  for the leaves; and  $Fe > Zn > Mn$  for fruits (Table [2](#page-4-0)). According to Kirkby ([2012\)](#page-14-2), the average concentrations of mineral elements in plant shoot dry matter sufficient for adequate growth are 100 mg kg<sup>-1</sup> of Fe, 50 mg kg<sup>-1</sup> of Mn, and 20 mg kg<sup>-1</sup> of Zn, resulting in following order: Fe>Mn>Zn, similar to what was found in the leaves of the evaluated plants. The average concentration of



<span id="page-4-0"></span>**Table 2** Descriptive statistics and Shapiro–Wilk test for heavy metals contents in diferent parts of cultivated and native plants in "gossan" infuence area in the municipality of Lapão, Bahia, Brazil



 ${}^aC.V.$  = Coefficient of variation

 $b$ <LD = below detection limit

 $c***=p\leq 0.01$ 

Fe (319.5 mg kg<sup>-1</sup>) and Zn (34.1 mg kg<sup>-1</sup>) in the leaves of the evaluated plants was, respectively, around 3.2 and 1.7 times higher than those indicated by Kirkby ([2012\)](#page-14-2), while the average concentration of Mn (49.2 mg kg<sup>-1</sup>) was pretty similar. The same author points out that the values can vary considerably depending on plant species, plant age, and concentration of other mineral elements.

In addition, the wide variation around the average, evidenced by the high values of the coefficients of variation (equal to or greater than 80%), considered high according to Gomes ([1984\)](#page-14-24), may have afected the results. Such results were already expected due to the sample character of the study, in which parts of diferent plant species were sampled at diferent growth stages, thus resulting in a high variability for all heavy metals, where the lowest coefficient of variation was observed for Mn on the leaf (80%) and the highest (653%) for Cr on the leaf. Confrming this, the data obtained did not follow a normal distribution, according to the Shapiro–Wilk test used (Table [2\)](#page-4-0).

## **Distribution of heavy metal in diferent parts of the plants**

In this topic, the distribution of Pb, Fe, Mn, Ti, Zn, Cu, and Cr in diferent parts of evaluated plants will be discussed (Tables [3,](#page-5-0) [4](#page-5-1), [5](#page-6-0), [6](#page-7-0) and [8,](#page-10-0) [9](#page-11-0), [10](#page-12-0)). As previously mentioned, the concentration of As, Cd, and Ni was below the detection limit and therefore will not be discussed. The data for the elements that will be discussed are being presented only for the species that showed a concentration above the detection limit for at least one part of the plant.

Among the seventeen species evaluated, ten of them (59%) presented Pb levels above the detection limit in some of the parts of the plants, and these levels ranged from 0.05 to 24.31 mg kg<sup>-1</sup>. According to Kabata-Pendias  $(2011)$  $(2011)$ , these values are below that those one considered as toxic to plants, which vary between 30 and 300 mg kg<sup>-1</sup>. Regarding the distribution of Pb in the diferent parts of the plants, there is a clear trend of accumulation of this element in the roots, evidenced by the distribution coefficients of the element (DC) for each evaluated part (Table [3](#page-5-0)). Of the ten species, seven of them (angico, corn, forage cactus, white pinion, custard apple, red mombin, and hog plum) presented a DC for 1.000 for roots, indicating that the Pb was not transported to other parts of the plants. Similar behavior occurred with the buffel grass, which had a DC of 0.998 for roots and 0.002 for leaves. Another specie that tended to accumulate Pb in the roots was bean. Even though this behavior is less evident than that of the crops previously mentioned, the bean showed a DC for root of 0.646 and 0.354 for leaves. Out of



<span id="page-5-0"></span>**Table 3** Average levels of Pb in diferent parts of cultivated and native plants in "gossan" influence area in the municipality of Lapão, Bahia, Brazil



<sup>a</sup>Distribution coefficient of heavy metal in different plants parts in relation to the total of each plant b Below detection limit

c No fruits at the sampling time



<sup>a</sup>Distribution coefficient of heavy metal in different plants parts in relation to the total of each plant

b Below detection limit

c No fruits at the sampling time



<span id="page-5-1"></span>**Table 4** Average levels of Ti in diferent parts of cultivated and native plants in "gossan" influence area in the municipality of Lapão, Bahia,

Brazil

<span id="page-6-0"></span>**Table 5** Average levels of Cr in diferent parts of cultivated and native plants in "gossan" influence area in the municipality of Lapão, Bahia, Brazil



<sup>a</sup>Distribution coefficient of heavy metal in different plants parts in relation to the total of each plant

b Below detection limit

c No fruits at the sampling time

the group that showed a tendency for Pb accumulation in the roots, the castor bean showed a tendency for Pb accumulation in the stem with a DC of 1.000.

The highest percentage of Pb in the roots of the evaluated species might be resulting from diferent factors. For Alloway ([1990\)](#page-14-25), the Pb translocation is infuenced by the plant status in terms of growth and development. In optimal growing conditions, Pb precipitates in the roots cell walls as little soluble compounds, with small amounts transported to the leaves and fruits. The author also noted that the Pb absorption and translocation Pb may be infuenced by season, where in autumn and winter, there is a greater translocation to the aerial part than in other seasons.

The behavior of Ti (Table [4\)](#page-5-1) was pretty similar to Pb in terms of the percentage of occurrence among the species and distribution among the diferent parts of the plants. Ti levels above the detection limit were observed in nine of the seventeen species evaluated, indicating a percentage of occurrence in 53% of the species. Ti levels ranged from 0.34 to 20.83 mg kg−1. According to Kabata-Pendias [\(2011\)](#page-14-1), Ti content in plants has a quite considerable variation in the range of 0.15–80 mg  $kg^{-1}$  in most plants, reaching values of up to 1500 mg kg<sup>-1</sup> in diatoms. Wallace et al.  $(1977)$  $(1977)$ observed toxicity Ti symptoms in the form of chlorotic and necrotic spots on bean leaves containing concentration about 200 mg  $kg^{-1}$ . Ti is still far from being accepted as an essential element for plants (Wild and Jones [1988](#page-15-1)), but there are some reports of its benefcial efects on the various crop productions. Although little research has been done about Ti absorption by plants, this element is considered relatively little available to plants and not easily mobile in vegetal tissues (Simonete et al. [2003](#page-14-26)). Of the nine species in which Ti was detected, five of them (aroeira tree, corn, forage cactus, white pinion, and red mombin) concentrated the element in its roots ( $DC = 1.000$ ) (Table [4\)](#page-5-1). The buffel grass also showed a large part of the Ti accumulated in the roots  $(DC=0.862)$ ; however, it was possible to detect the element in the stems ( $DC = 0.079$ ) and in the leaves ( $DC = 0.059$ ). On the other hand, banana ( $DC = 1.000$ ), bean ( $DC = 0.739$ ), and castor been  $(DC=0.762)$  showed a higher concentration of Ti in the leaves.

The results for Pb and Ti reveal the low possibility of those elements entering in the food chain, both by the small number of species that absorbed the elements and by the accumulation in the roots even when there was absorption. In general, the root is the part of the plant that is not normally consumed by humans, except in some crops like cassava.

Among the evaluated elements, Cr was the heavy metal found in smallest number of species among all studied. In the group of seventeen evaluated species, only three of them (18%) presented Cr in any of the parts of the plants with lev-els ranging from 0.19 to 33.26 mg kg<sup>-1</sup> (Table [5\)](#page-6-0), with a distinct standard of Cr distribution among the species in their respective parts. For corn, it was possible to observe most of the Cr accumulated in the roots  $(CD=0.883)$  and a smaller part in the stems  $(CD=0.117)$ . In the buffel grass, there was a tendency to accumulate in the roots  $(Cd=0.464)$  and in the fruits  $(CD=0.431)$ , in addition to the small accumulation in the stem  $(CD=0.054)$  and in the leaves  $(CD=0.051)$ . The "aroeira" tree was the only species that showed Cr completely concentrated in the leaves  $(DC=1.000)$ , indicating intense Cr transport from the roots to the aerial part of the plant. The behavior of Cr in the "aroeira" tree draws attention due to the fact that this element is described in the literature as not easily translocated within plants; thus, it is concentrated mainly in roots (Kabata-Pendias [2011](#page-14-1)). The value observed in "aroeira" tree  $(33.26 \text{ mg kg}^{-1})$  is above those found by Malavolta [\(1976](#page-14-27)), which cited maximum values of Cr in dry matter ranging from 3.9 to 14.8 mg kg<sup>-1</sup>, but without mentioning phytotoxic levels. For the other species, values close to those found by Ritter and Eastburn [\(1978\)](#page-14-28) were observed, after applying sewage sludge on a silty loam soil, with Cr concentrations less than 1.0 mg  $kg^{-1}$  in the grains and between 1.0 and 2.0 mg  $kg^{-1}$  in the corn stalks.



Common name	Scientific name	Units	Fe				
			Roots	Stems	Leaves	Fruits	Total
Angico	Anadenthera colubrina	$mg \, kg^{-1}$	270.61	$\rm <\!LD^b$	36.45	16.49	323.55
		$DC^a$	0.836		0.113	0.051	1.000
"Aroeira" tree	Myracrodruon urundeuva	$mg \, kg^{-1}$	1172.82	$\langle L \rangle$	372.14	$\rm{NF}^c$	1544.96
		DC	0.759		0.241		1.000
Banana	Musa spp.	$mg \, kg^{-1}$	34.46	134.76	1486.57	19.94	1675.73
		DC	0.021	$0.080\,$	0.887	0.012	$1.000\,$
<b>Buffel</b> grass	Cenchrus ciliaris	$mg \, kg^{-1}$	1457.03	341.2	288.58	212.02	2298.83
		DC	0.634	0.148	0.126	0.092	$1.000\,$
Bean	Phaseolus vulgaris	$\rm mg~kg^{-1}$	484.64	88.84	641.64	121.82	1336.94
		DC	0.362	0.067	0.480	0.091	1.000
"Jurema preta" tree	Mimosa tenuiflora	$mg \, kg^{-1}$	550.42	39.66	192.58	NF	782.66
		DC	0.703	0.051	0.246		1.000
Castor bean	Ricinus communis	$mg \, kg^{-1}$	312.34	58.19	659.78	NF	1030.31
		DC	0.303	0.057	0.640	$\overline{\phantom{0}}$	$1.000\,$
"Mandacaru"	Cereus jamacaru	$mg \, kg^{-1}$	414.15	$\rm L$	$\rm <\!LD$	$\rm NF$	414.15
		DC	$1.000\,$	$\overline{\phantom{0}}$	$\qquad \qquad -$	$\qquad \qquad -$	$1.000\,$
Corn	Zea mays	$mg \, kg^{-1}$	1871.53	120.48	252.75	$\rm NF$	2244.76
		DC	0.833	0.054	0.113	$\overline{\phantom{0}}$	$1.000\,$
"Mucambo" tree	Balfourodendron riedelianum	$mg \, kg^{-1}$	177.22	146.34	284.08	$\rm NF$	607.64
		DC	0.292	0.241	0.467	$\overline{\phantom{0}}$	$1.000\,$
Forage cactus	Opuntia ficus-indica	$\rm mg~kg^{-1}$	1024.07	75.3	75.3	NF	1174.67
		$DC$	0.872	0.064	0.064	$\equiv$	1.000
White pinion	Jatropha spp.	$\rm mg~kg^{-1}$	1795.05	54.55	198.36	NF	2047.96
		DC	0.876	0.027	0.097	$\qquad \qquad -$	1.000
Custard apple	Annona squamosa	$mg \, kg^{-1}$	533.09	6.86	118.33	11.09	669.37
		DC	0.796	0.010	0.177	0.017	$1.000\,$
"Quebra-facão" tree	Hymenaea courberil	$mg \, kg^{-1}$	493.08	7.93	171.19	NF	672.2
		DC	0.733	0.012	0.255		1.000
Red mombin	Spondias purpurea	$mg \, kg^{-1}$	1082.49	18.82	39.87	16.76	1157.94
		DC	0.935	0.016	0.034	0.015	1.000
Hog plum	Spondias spp.	$mg \, kg^{-1}$	263.31	$\rm L$	26.72	$_{\rm NF}$	290.03
		DC	0.908	$\overline{\phantom{0}}$	0.092	$\overline{\phantom{0}}$	$1.000\,$
"Umburaninha" tree	Commiphora leptophloeos	$mg \ kg^{-1}$	349.28	150.11	594.29	34	1127.68
		DC	0.310	0.133	0.527	0.030	1.000

<span id="page-7-0"></span>**Table 6** Average levels of Fe in diferent parts of cultivated and native plants in "gossan" infuence area in the municipality of Lapão, Bahia, Brazil

<sup>a</sup>Distribution coefficient of heavy metal in different plants parts in relation to the total of each plant

b Below detection limit

c No fruits at the sampling time

The Fe element was detected in at least one part of the seventeen evaluated species with a content ranging from 6.86 to 1871.53 mg kg<sup>-1</sup> (Table [6](#page-7-0)). As with other metals, Fe was accumulated mainly in the roots of the plants. Considering the seventeen species evaluated, the DC was higher for the root than for other parts of the evaluated plants in twelve of them (71%), being that in one of the species, the element was totally concentrated in the root (mandacaru –  $DC = 1.000$ ), and in the other species, the distribution coefficients were

above 0.634. The other fve species (banana, bean, castor bean, "Mucambo" tree, and "Umburaninha" tree) showed a tendency to accumulate Fe in leaves with CD ranging from 0.467 to 0.887.

PCA analysis revealed that PCs 1 and 2 explained 82% of the data variation on the Fe levels distribution in diferent parts of the plants (Table [7](#page-8-0)). About 52% of the variation explanation was given by PC1, whose eigenvectors with the highest correlations were those referring to roots,



Variable	Cu		Fe		Mn		Zn	
	PC <sub>1</sub>	PC2	PC1	PC <sub>2</sub>	PC <sub>1</sub>	PC <sub>2</sub>	PC1	PC2
Roots	0.38466	$-0.66913$	0.76748	$-0.54648$	0.91851	$-0.22963$	0.86194	$-0.20221$
<b>Stems</b>	$-0.86255$	$-0.28793$	$-0.49640$	$-0.79852$	0.08071	$-0.93893$	0.81622	$-0.33000$
Leafs	$-0.85527$	$-0.31279$	$-0.78479$	$-0.38395$	$-0.63490$	$-0.42479$	0.85271	0.29678
Fruits	0.39356	$-0.65680$	0.79533	$-0.34990$	0.91064	0.01867	0.20116	0.94744
Eigenvalues	1.78	1.06	2.08	1.21	2.08	1.12	2.18	1.14
Explained variance $(\%)$	44.46	26.50	52.10	30.15	52.06	27.88	54.42	28.39
Accumulated variance $(\%)$	44.46	70.95	52.10	82.25	52.06	79.94	54.42	82.81

<span id="page-8-0"></span>**Table 7** Eigenvalues and accumulated variance obtained in the principal component analysis (PCA) from the heavy metals contents in diferent parts of cultivated and native plants in "gossan" infuence area in the municipality of Lapão, Platô de Irecê, Bahia, Brazil

leaves, and fruits. The species with the highest levels of Fe in the leaves were bananas and beans (Fig. [1](#page-9-0)a), both collected in Z4 position, that is, further away from the "gossan" center. Kumar and Chopra ([2013\)](#page-14-29) observed the highest Fe levels in bean leaves grown in soil treated with sewage sludge in relation to other plant organs. The bufel grass, whose collection took place in the "gossan" central zone (Z1), showed a strong correlation with Fe levels in the roots and in the fruits (seeds). The other species, collected in the diferent zones, showed greater variation as to the location of the highest Fe concentration in the plant, correlating more strongly with PC2.

The large accumulation of Fe, Ti, and Pb in the roots shows that this is the main part of plants that accumulates heavy metals (McBride [1994](#page-14-30)). This root heavy metals concentration, without translocating them to the aerial part, has the positive aspect to avoid or minimize the organisms contamination that feed on aerial part of these plants; the opposite was found by Kumar and Chopra ([2013](#page-14-29)), who observed the highest Fe levels in bean leaves grown in soil treated with sewage sludge in relation to other parts.

In terms of occurrence in the species evaluated, Mn behaved like Fe, being possible to detect it in the seventeen species evaluated, with a content ranging from 0.74 to 163.05 mg  $kg^{-1}$  (Table [8](#page-10-0)). Unlike Pb, Ti, and Fe, in which the accumulation of those metals for most of the evaluated species occurred mainly in the root, the Mn accumulated mainly in the leaves. Of the seventeen species evaluated, twelve of them (71%) had a DC for leaves greater than for other parts of the plants. Although the Mn is one of the most abundant metals in the lithosphere (Kabata-Pendias [2011\)](#page-14-1), it was the third element in higher concentration found in the studied species, mainly in leaves and roots, followed by stems and with lower concentration in fruits (Table [8](#page-10-0)), showing the element distribution in all parts of evaluated species. In cultivated crops, it is observed that the Mn leaves and fruits levels were below or close to the values reported by Kabata-Pendias [\(2011](#page-14-1)) for plant foods, with the highest

values in beet roots (36–113 mg kg<sup>-1</sup>) and the lowest in fruit of trees  $(1,3 \text{ a } 1,5 \text{ mg kg}^{-1})$ .

For Webber et al. [\(1984](#page-15-2)), Mn contents considered phytotoxic in corn leaf are from 100 to 150 mg  $kg^{-1}$ . In this study, it can be seen that it was found content below this range, i.e., 60.[8](#page-10-0)6 mg kg<sup>-1</sup> (Table 8). For grains produced in sites contaminated by the metal, the critical value established by Kabata-Pendias ([2011\)](#page-14-1) was between 15 and 80 mg kg<sup>-1</sup>. Excepting banana, buffel grass, and bean, these levels were not found in the other studied fruits (Table [8](#page-10-0)). According to Silva [\(1999](#page-14-31)), the Mn leaves content of 93.54 mg kg<sup>-1</sup> is sufficient for the adequate supply to plants without causing phytotoxic levels. In this study, this value was exceeded by the white pinion (163.05 mg kg<sup>-1</sup>) and "umburaninha tree"  $(97.44 \text{ mg kg}^{-1})$  (Table [8\)](#page-10-0).

About 80% of the data variation referring to Mn distribution in the diferent plants parts was explained by PCs 1 and 2 (Table [7](#page-8-0)). The eigenvectors referring to the Mn concentration in fruits and roots correlated positively with PC1, which explained 52% of data variation (Fig. [1](#page-9-0)b). Bufel grass, collected in the "gossan" center, and banana, collected in Z4 position, were those that most concentrated Mn in fruits and roots. Other species showed a tendency to concentrate more Mn in the stem, such as corn, both from plants collected in the "gossan" center or in a more distant position (Z4). Corn showed this clear diference in relation to the other species regarding the stem Mn accumulation. Although with less explanation in relation to fruits and roots, species such as beans showed a strong correlation with the eigenvector referring to leaves, which indicates that this plant part is where the highest Mn content is concentrated.

The Zn levels in the diferent parts of the evaluated spe-cies ranged from 0.44 to 218.38 mg kg<sup>-1</sup> (Table [9\)](#page-11-0), being that some of these values are between the levels considered phytotoxic cited by Kabata-Pendias ([2011\)](#page-14-1), from 100 to 400 mg  $kg^{-1}$ . As with Mn, most species showed greater accumulation of Zn in the leaves. However, one must also consider the greater accumulation of Zn in the fruits. Of the seven species that showed fruit at the time of collection, fve





<span id="page-9-0"></span>**Fig. 1** Biplot diagram from principal component analysis (PC1 and PC2) for metals distribution in plant parts of diferent species collected in the center (Z1), at 100 (Z2), 200 (Z3), and 400 (Z4) meters from the "gossan" center in north (N) and south (S) directions. Sam-

pled species were: ban=banana tree; bea=common beans; buf=buffel grass; cast=castor bean; cust=custard apple; maiz=maiz tree; spon=*Spondias* spp. Ex. Z3bea\_N: common bean plant collected at 200 meters from the "gossan" center in the north direction

of them accumulated more Zn in the fruit than in any other part of the plant. The results obtained are not in accord-ance with Dechen et al. ([1991](#page-14-32)), which concluded that the roots concentrate more Zn than the aerial part. Some authors consider Zn as highly mobile in plants, while others consider it having intermediate mobility, being distributed to all plants parts. Analyses of parts of the plants from angico, bufel grass, bean, corn, and castor bean showed



<span id="page-10-0"></span>**Table 8** Average levels of Mn in diferent parts of cultivated and native plants in "gossan" influence area in the municipality of Lapão, Bahia, Brazil



<sup>a</sup>Distribution coefficient of heavy metal in different plants parts in relation to the total of each plant b Below detection limit

c No fruits at the sampling time

Zn levels found in the roots, stems, and leaves (Table [9\)](#page-11-0) revealing intense transport activity in the plant (Malavolta [1994](#page-14-33); Berton [2000](#page-14-34)). For leaves, the Zn levels found in the species evaluated are within the range of  $15–100$  mg kg<sup>-1</sup> considered appropriate by Raij et al. [\(1996](#page-15-3)). However, if one considers the range of 15 to 50 mg  $kg^{-1}$ , proposed by Malavolta et al. ([1989](#page-14-35)), the level found in the bufel grass leaves (75.32 mg kg<sup>-1</sup>) is within the phytotoxicity range. Zn is considered a metal with low-to-moderate phytotoxicity (Kabata-Pendias [2011\)](#page-14-1).

Data variation referring to the Zn in plants was explained in about 83% by PCs 1 and 2 (Table [7](#page-8-0)). The greatest data <span id="page-11-0"></span>**Table 9** Average levels of Zn in diferent parts of cultivated and native plants in "gossan" influence area in the municipality of Lapão, Bahia, Brazil



<sup>a</sup>Distribution coefficient of heavy metal in different plants parts in relation to the total of each plant

b Below detection limit

c No fruits at the sampling time

explanation was given by PC1 (54%), showing that Zn was more concentrated in the roots, stems, and leaves (Fig. [1c](#page-9-0)). Among the species evaluated, corn was the one that stood out from the others, correlating more strongly with the eigenvectors referring to the roots and stems, both in plants collected close (Z1) or distant (Z4) to the "gossan" center. Bufel grass, on the other hand, seemed to concentrate more Zn in the seeds, which can be seen by the strong correlation it has with the eigenvector related to the fruits, which, in turn, was more strongly correlated with PC2, which explained about 28% of data variation.

Cu was found in diferent plants and in diferent parts of them, for example, bufel grass and corn roots, bean and corn stems, "aroeira" tree, bean, and corn leaves, and buffel grass, bean, and red mombin fruits (Table [10\)](#page-12-0). Higher Cu concentration occurred in corn roots (distribution coefficient of 0.600), and it has decreased along the other parts, confrming the behavior observed by other authors that the <span id="page-12-0"></span>**Table 10** Average levels of Cu in diferent parts of cultivated and native plants in "gossan" influence area in the municipality of Lapão, Bahia, Brazil



<sup>a</sup>Distribution coefficient of heavy metal in different plants parts in relation to the total of each plant

b Below detection limit

c No fruits at the sampling time

low uptake of Cu by the plant can be attributed to their high affinity with the organic matter of the root tissue. The big diference between Cu concentrations in aerial parts and in roots, as seen in the corn, suggests that the plant has a mechanism that reduces the Cu difusion through the tissues, protecting them from intoxication. Due to this feature of Cu accumulating in the roots, perhaps this is the most suitable plant tissue to evaluate soil contamination degree by this metal (Marsola et al. [2005](#page-14-36)). The results for all other valued plants did not clearly express the Cu distribution in them, not confrming the results obtained by other authors.

Cu did not reach phytotoxicity levels in any of the parts of the plants evaluated. The maximum concentration observed was 1.72 mg  $kg^{-1}$  in the corn root (Table [10](#page-12-0)). According to Marschner ([1995\)](#page-14-37), the Cu phytotoxic contents are 20–30 mg kg<sup>-1</sup> in the leaves dry matter.

Data variation referring to the Cu in diferent plants parts was explained in about 71% by PCs 1 and 2 (Table [7\)](#page-8-0). The eigenvectors related to stem and leaves were more strongly

<span id="page-12-1"></span>**Table 11** Spearman's linear correlation coefficient between average heavy metal contents in diferent parts of cultivated and native plants and two soil layers<sup>a</sup>



a Results for As, Cd, and Ni metals are not displayed because the plant data were below the detection limit  $(<$ LD $)$ 

 $<sup>b</sup>p$  ≤ 0.05</sup>



correlated with PC1, indicating that these structures were the ones that presented the highest Cu levels (Fig. [1d](#page-9-0)). The vectors corresponding to the roots and fruits explained only about 26% of the data variation, being more correlated with PC2. Bean and corn, collected in Z4 and Z2 positions, respectively, showed higher levels of Cu in the stems and leaves, as can be seen by the strong correlation with these eigenvectors (Fig. [1d](#page-9-0)). Buffel grass collected in the "gossan" center showed a positive correlation with the Cu content in the roots and fruits, and corn in Z4 position showed a positive correlation with the Cu content in the roots, indicating a higher content of this metal in these specifc plants parts.

Plants have cellular mechanisms that act in response to metal excess resulting in detoxifcation or tolerance to them. The barriers formation at the root level by heavy metals immobilization in the cell wall or by the extracellular carbohydrates (mucilages, callose, pectins, and histidines) action is mechanisms that reduce the presence of free ions and their transfer to aerial part. So, roots metals accumulation occurs, with low aerial part concentration. Chelating agents (phytochelatins, organic acids, and amino acids) action is another mechanism responsible for forming complexes that reduce the heavy metals solubility and reactivity and therefore contribute to stress plants tolerance caused by them (Hall [2002](#page-14-38); Santos et al. [2006\)](#page-14-39). Those mechanisms explain the roots concentration of several heavy metals evaluated in this work, as Pb, Fe, Ti, Cu, and Cr, in diferent cultivated and native plants, with low or zero concentrations in the aerial part. The reverse occurred with Mn and Zn metals, with a higher aerial part concentration.

The results obtained in this work showed possible toxicity for Cr and possibly Zn. However, whereas the assessed area has been used for decades by small family farmers for bean, corn, castor bean, custard apple, forage cactus, red mombin, hog plum production and other crops and for raising small animals (goats, sheep, and chickens), fortunately the highest heavy metals concentration was observed in the roots of both cultivated and native plants.

## **Correlation between heavy metals contents in the soil and in diferent parts of plants**

The linear correlation study was used to evaluate the relationship between the metals content in diferent parts of the plants and in the soil. As previously indicated, the data obtained for plant and soil did not follow the normal distribution. For this reason, Spearman's linear correlation test was used to evaluate the data.

It was worthy to note the signifcant and positive correlation coefficient between Pb in root and in soil, and significant negative in the case of Pb in stem and leaf (Table [11\)](#page-12-1), indicating that the Pb content in root increased with its increase in soil, concentrating at the roots (Table [3](#page-5-0)). Similar behavior has occurred in relation to Cu, in the case concentrating at the root and fruit. Correlations involving other heavy metals do not indicate any aspect that deserve comment.

## **Conclusion**

Among the species evaluated, corn and buffel grass were those with the greatest capacity to indicate the metals distribution behavior in the plant, regardless of whether they were collected closer or further from the "gossan" center. The parts of the plants with the highest Cu, Fe, and Zn concentration were the roots and fruits. Zn highest concentrations seem to occur more in roots and stems for corn and in fruits for buffel grass. As and Cd were not detected in any part of the plants of the species evaluated. Buffel grass deserves special attention in the case of Cr, with its presence in all parts of the plants, but concentrated in roots and fruits. In corn, Cr was concentrated in the roots, with little presence in the stem. The presence of Pb and Ti was practically restricted to the roots, although Ti has been verified in leaves of some species as banana, bean, and castor bean. Pb traces were not observed in the other parts of the plants. Once again buffel grass was a sensitive specie to the environment heavy metals presence, since the content of 192 mg  $kg^{-1}$ of Pb in the roots was recorded in a sample collected in the "gossan" center, that is, about 77 times more in relation to the average content found in the other species. The results obtained in this work showed possible toxicity for Cr and Zn. However, whereas the assessed area has been used for decades by small family farmers for bean, corn, castor bean, custard apple, forage cactus, red mombin, hog plum production and other crops and for raising small animals (goats, sheep, and chickens), fortunately the highest heavy metals concentration was observed in the roots of both cultivated and native plants.

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