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Fractionation of heavy metals in yellow latosol cultivated with vegetables

Fracionamento de metais pesados em latossolo amarelo sob cultivo de hortaliças

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Abstract

Sequential extraction or chemical fractionation of heavy metals allows inferences to be made about their origin, occurrence, bioavailability, toxic potential and environmental contamination. Thus, the present study aimed to assess the distribution of Cu, Mn, Ni, Pb and Zn among the different soil fractions and landscape compartments of a yellow latosol cultivated with vegetables. Soil samples were collected from five areas cultivated with tomato (*Lycopersicon esculentum*, Mill.), lettuce (*Lactuca sativa*), chili pepper (*Capsicum annuum* L.) and chard (*Beta vulgaris* L.) in different slope positions (upper, middle, lower), and four reference areas (native forest), at a depth of 0.00 - 0.20 m. Heavy metal levels were also assessed in water used to irrigate the crops and for human consumption by collecting 200 ml of water samples from reservoirs. The soil samples were sequentially fractionated to quantify the concentrations of adsorbed Cu, Mn, Ni, Pb and Zn in the exchangeable (*EF*), organic matter (*OF*), amorphous and crystalline iron oxide fractions (*AFeOx* and *CFeOx*). Landscape position only interfered significantly in heavy metal adsorption in the soil for Cu and Ni associated with *CFeOx* and Zn bound to the *EF* in the farming areas. The highest Cu, Ni, Pb and Zn levels were found in the fractions with less stable chemical bonds (bound to organic matter), in addition to a strong affinity between Cu, Zn and Mn and the oxide fractions (*AFeOx* + *CFeOx*). The low affinity of Pb and Ni for the *AFeOx* and *CFeOx* fractions indicates greater contamination potential for the water reservoirs. In the short term, organic matter is the main source of remediation for heavy metal contamination in soil, making it important to adopt conservation practices aimed at reducing OM losses.

Key words: Chemical extraction. Soil contamination. Soil pollution. Environmental monitoring.

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Resumo

Extrações sequenciadas ou fracionamento químico de metais pesados permitem inferências sobre origem, forma de ocorrência, biodisponibilidade, potencial de toxicidade e contaminação ambiental por esses elementos. Assim, o presente estudo foi desenvolvido com o propósito de avaliar a distribuição de Cu, Mn, Ni, Pb e Zn entre as diferentes frações do solo e compartimento da paisagem, de um Latossolo Amarelo sob cultivo de hortaliças. Foram coletadas amostras de solos de cinco áreas cultivadas com tomate (*Lycopersicon esculentum*, Mill.), alface (*Lactuca sativa*), pimentão (*Capsicum annuum* L.) e acelga (*Beta vulgaris* L.) em diferentes posições no relevo (topo, encosta, baixio) e quatro áreas de referência (mata nativa), na profundidade de 0,00 - 0,20 m. Também foram avaliados os teores de metais pesados na água destinada à irrigação das lavouras e ao consumo humano, coletando-se para isso, 200 ml de amostras de água dos reservatórios. As amostras de solo foram fracionadas sequencialmente para quantificação dos teores de Cu, Mn, Ni, Pb e Zn adsorvidos às frações trocável (*FT*), matéria orgânica (*FO*), óxido de ferro amorfo e cristalino (*OxFeA* e *OxFeC*). As posições da paisagem interferiram significativamente na adsorção de metais pesados no solo apenas para o Cu e o Ni ligados à *OxFeC* e para o Zn ligado à *FT*, nas áreas cultivadas. Os maiores teores de Cu, Ni, Pb e Zn no solo encontram-se nas frações com ligações químicas menos estáveis (ligados à matéria orgânica) sendo também encontrada forte afinidade de Cu, Zn e Mn às frações oxídicas (*AFeOx* + *CFeOx*). A baixa afinidade de Pb e Ni às *OxFeA* e *OxFeC* condiciona maior potencial de contaminação dos reservatórios hídricos. A curto prazo, a matéria orgânica é a principal fonte de remediação de metais pesados no solo, sendo importante a adoção de práticas conservacionistas que reduzam suas perdas.

Palavras-chave: Extração química. Contaminação de solo. Poluição de solo. Monitoramento ambiental.

Introduction

The worldwide increase in anthropogenic, industrial and agricultural activities is responsible for the growing release of different pollutants into the environment (KABATA-PENDIAS, 2010; MACEDO et al., 2012; SILVA et al., 2016). Heavy metals such as cadmium (Cd), copper (Cu), manganese (Mn), nickel (Ni), zinc (Zn) and lead (Pb) are the most well-known and cause significant damage to the environment and human health. Farming in soils that are subject to intensive fertilizer and pesticide application and poor quality irrigation water (SILVA et al., 2016) are the main entry routes for these metals into human and animal diets (CHANEY; OLIVER, 1996; FERNANDES et al., 2007; CONAMA, 2009; ATSDR, 2011).

The number of people with diseases and health issues related to heavy metal contamination is growing. In the United States, more than 500,000 people are exposed to Cd every year according to the Agency for Toxic Substances and Disease Registry (ATSDR, 2008). In China, about 10 million ha of arable land has been polluted and 12 million metric tons of grain is contaminated every year due to the presence of heavy metals in the soil (TENG et al., 2010). Also in China, 3.4×10^{-3} mg kg^{-1} of As, Cr, Cd and Ni were found in the city of Guangdong, levels far above the standard range of 1×10^{-6} to 1×10^{-4} mg kg^{-1}, indicating a significant cancer risk for the population by consuming contaminated water and vegetables, particularly leafy varieties (LIANG et al., 2017).

Given their toxicity to living beings, persistence and accumulation in the ecosystem, heavy metals are considered extremely hazardous (NAGAJYOTI et al., 2010; ATSDR, 2011; SHENG et al., 2012). In the soil, these metals can be found in different chemical forms and at concentrations that are not fully available to plants (KABALA; SINGH, 2001). Some authors have reported that the concentration and distribution of metals in soil depends primarily on the geochemical nature of the parent material (KABALA; SZERSZEN, 2002; BIONDI et al., 2011; ALMEIDA JÚNIOR et al., 2016; SILVA et al., 2016). In turn, their potential toxicity and mobility are heavily influenced by the intensity of adverse weather conditions, soil mineralogy, pH, and cation exchange capacity (CEC), as well as the texture and content of the parent material (HAN et al., 2001; NACHTIGALL et al., 2009; LIMA et al., 2013). As such, it is important to investigate which soil compartment these metals are associated with in order to plan safe and appropriate interventions to mitigate future environmental impacts.

One of the most widely used techniques is chemical fractionation, commonly known as sequential extraction, whereby the same sample is sequentially treated with extractors, moving from the least to most aggressive, with the same procedure applied for temperature and agitation (VIETS JUNIOR, 1962). This method is used to determine the proportions associated with the fractions that are most labile (soluble, exchangeable, associated with carbonate), more stable (lower mobility and/or bioavailability), and bound to Fe and Mn, organic matter and the residual fraction (KABATA-PENDIAS, 2010). Heavy metal fractionation makes it possible to predict bioavailability and the potential mobility, leaching and contamination of soil (LIMA et al., 2013). As such, this technique can contribute to proper management practices and the planning of agricultural activities responsible for the rise in heavy metal levels in soil through the indiscriminate use of pesticides (SILVA et al., 2016).

Several studies have elucidated the behavior of heavy metals in soil fractions (RAMALHO et al., 2000; FERNANDES et al., 2007), but a number of more recent investigations were limited to conducting pot experiments (ANDRADE et al., 2009b; FREITAS et al., 2009; LIMA et al., 2013) or using residues (SOARES REIS et al., 2014). However, there is still a shortage of studies that consider the influence of landscape on spatial distribution, particularly in the agroecosystem (SILVA et al., 2016). In light of the above, the present study aimed to assess the distribution of Cu, Mn, Ni, Pb and Zn among the different soil fractions and landscape compartments of a yellow latosol cultivated with vegetables.

Material and Methods

The study was conducted in vegetable farming areas in the municipality of Camocim de São Félix, located in the southern Agreste region of Pernambuco state, in the Brejo Pernambucano microregion, Brazil. The predominant climate in the microregion is As, according to the Köppen-Geiger classification system, with a rainy tropical climate and dry summer. The average annual temperature is around 24 °C, ranging from 20 to 22°C in the coldest month, with annual rainfall between 900 and 1300 mm. Altitudes exceed 600 m, but rarely surpass 1000 m, with an undulating to sharply undulating relief, highly to moderately developed soil and deep natural vegetation consisting primarily of deciduous and/or semi-deciduous forests (VIEIRA, 2011).

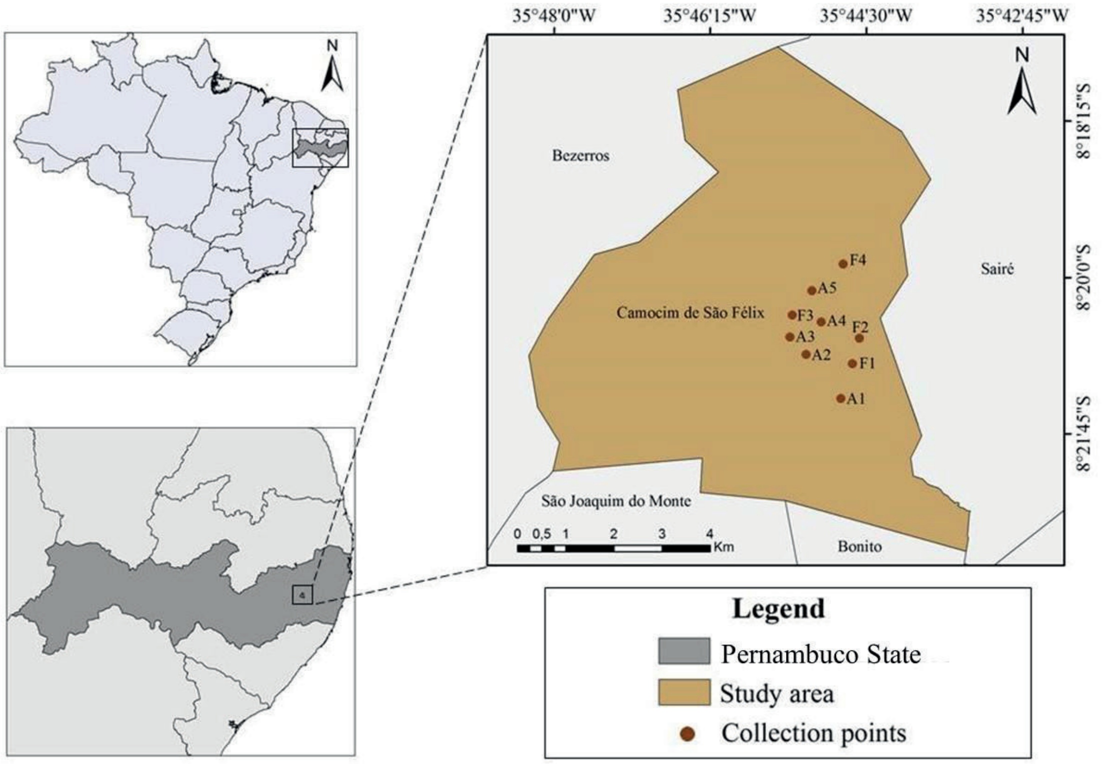
The soil at the different sampling sites is classified as yellow latosol, according to the Brazilian system of soil classification - SiBCS (EMBRAPA, 2013), and xanthic ferralsol under the FAO classification (1990). With respect to geology, according to Brasil (1973), the soil developed from Precambrian rocks consisting of gneisses and granites, with sandy clay material on the surface of some soil.

The study was conducted between 2010 and 2012. Based on site visits and information obtained from the local branch of the Pernambuco Agronomic Institute (IPA) and rural farmers, we selected five farming areas (A1, A2, A3, A4 and A5) that have been growing vegetables for more than 35 years, with the predominant crops being tomato (*Lycopersicon esculentum*, Mill.), lettuce (*Lactuca sativa*), chili pepper (*Capsicum annuum* L.) and chard (*Beta vulgaris* L). Management was similar for all the areas, with crops grown along the slopes at the following gradients: A1=31%, A2=33%, A3=32%, A4=33% and A5=32%. Each area has its own reservoir (R1, R2, R3, R4 and R5), located on the lowest portion of the slope, with the water used for crop irrigation and human consumption.

Given the poor chemical quality of the soil, that is, advanced pedogenesis, fertilizer is periodically applied, including monoammonium phosphate (MAP), diammonium phosphate (DAP), single superphosphate (SSP), triple superphosphate, magnesium thermophosphate, and different NPK formulations (06-24-12; 20-10-20; 10-10-10; 10-20-20 and 20-0-20). Organic waste in the form of crop residues and chicken manure is also incorporated into the soil. The preventive pesticides used belong to the following chemical groups: organophosphorus, isophthalonitrile, benzimidazole, azoxystrobin (strobilurin), cyproconazole (triazole), ethylene bis (dithiocarbamate), strobilurin, triazoles, dicarboximide, pyrethroid, benzofuranyl methylcarbamate, benzoylurea, diphenyl ether, N-substituted glycine.

A randomized block design was used to compare Cu, Mn, Ni, Pb and Zn levels between farming areas and landscape positions, whereby each area served as one block (A1, A2, A3, A4 and A5), with three treatments (upper, middle and lower slope) and a depth of 0.00 - 0.20 m. Four native forest areas (M1, M2, M3 and M4) were also assessed and served as a local reference to strengthen the arguments and conclusions, as well as identify the natural behavior of heavy metals in soil subject to anthropic influences, that is, their origin, and possible contamination risks. The forest areas were fragments of secondary forest vegetation in the upper section of the slops, with minimal anthropic intervention. Both the farming and forest areas were georeferenced using a Garmin eTrex Vista GPS device (Figure 1).

Figure 1. Location of the study area and sites representing the subareas sampled (A1, A2, A3, A4 and A5 = farming areas; F1, F2, F3, F4 = forest areas) in Pernambuco state.



In each of the farming areas, a total of 10 discrete soil samples were collected along the rows at a depth of 0.00 - 0.20 m, comprising one composite sample for each landscape position. Due to the presence of forest vegetation on the flat surface of the slope, samples were collected in a zigzag pattern at the same depth and only in the upper section, also totaling 10 discrete samples to form one composite sample. After air drying, the samples were broken up and sieved in a 2.00 mm mesh sieve to obtain air-dried fine earth (ADFE).

In this study, 200 mL of water was collected from the reservoirs every month, in addition to samples of domestically consumed water. Collections were performed between the 5th and the 8th day of each month (January to December) at different points of the reservoirs, avoiding areas with murky water or suspended material. Residential water was collected from an outlet on an artesian well. Five subsamples were collected to form a 200 mL composite sample. The sampling containers were previously immersed in acidic solution (3% HCl) for 24 hours, according to the methodology described by the American Public Health Association (APHA, 2012).

The water samples were immediately acidified using nitric acid diluted with 1 mL HNO_3 for every 100 mL of sample to preserve the chemical and biological properties of the water (APHA, 2012). Once sealed, the flasks were kept in coolers and transported to the laboratory. On the same day they were collected, the samples were filtered in the laboratory (slow filtering qualitative filter paper) to prevent the release of low levels of the elements from the particulate material into the solution, and stored in a refrigerator at 4 °C. When possible, the heavy metal levels in the water were compared to the guideline values recommended in Resolution 357/2005 (CONAMA, 2005).

Table 1 presents the soil chemical properties pH, Ca^{2+}, Mg^{2+}, K and P, determined according to the methods proposed by Embrapa (2011). Organic carbon was measured using the technique described by Walkley and Black (1934).

Table 1. Chemical characterization of soil from the three landscape compartments in areas used to grow vegetables and references areas (forest).

Attributes	Unit	Landscape Compartment			
		Upper Slope	Middle Slope	Lower Slope	Forest
		Depth 0.00-0.20 m			
pH	H_2O	5.8	6.2	5.8	4.6
Ca	$cmol_c\ dm^{-3}$	4.3	4.3	3.8	1.2
Mg	$cmol_c\ dm^{-3}$	2.3	2.2	1.5	2.6
P	$mg\ dm^{-3}$	170.2	206.2	150.4	6.8
K	$cmol_c\ dm^{-3}$	1.5	1.8	1.0	0.3
MO	$g\ kg^{-1}$	26.1	22.1	20.2	41.8

pH = Soil pH; Ca = calcium content; Mg = magnesium content; P = phosphorus content; K = potassium content; OM = organic matter; A = farming areas; M = forest areas; U = upper; M = middle; L = lower.

Soil texture was classified based on the soil textural triangle (EMBRAPA, 1997), with sand, silt and clay content varying from 210 - 520, 60 - 160 and 420 - 730g kg^{-1}, respectively, in cultivated soil, and 210 - 570, 60 - 210 and 370 - 610 g kg^{-1}, respectively, for forest soil. Thus, the soil studied was classed as sandy clay loam, sandy loam and sandy clay.

Fractionation was performed using 5 g samples of ground ADFE in 50 mL centrifuge tubes. The levels of Cu, Mn, Ni, Pb and Zn adsorbed to the exchangeable fraction, organic matter and crystalline iron oxides were obtained using the method described by Shuman (1985); in turn, heavy metals associated with the amorphous iron oxide fraction were determined in line with Chao and Zhou (1983).

Exchangeable Fraction - EF - 20 mL of the magnesium nitrate extractor ($Mg(NO_3)_2$) was added to the centrifuge tube at 1 mol L^{-1}. The tube was manually shaken to loosen the soil, submitted to 2 hours in a horizontal mechanical stirrer and then centrifuged for 10 min. The supernatant was filtered through fast filtering filter paper, placed in a capped flask and added with 20 mL of distilled water. The procedure was repeated, with 3 minutes of mechanical stirring.

Organic Matter Fraction - OF - After the previous process, the same sample was treated by adding 10 mL of the sodium hypochlorite extractor (NaClO 5%, adjusted to basic pH 8.5 at the moment of addition) to the 50 mL centrifuge tube. Given its high instability, the solution was corrected using concentrated HCl. The tube was manually shaken to loosen the soil and centrifuged for 10 min at 2000 rpm, then placed in a water bath at 100ºC for 30 min, and returned to the centrifuge for a further 10 min. The supernatant was filtered (blue band) immediately to prevent readsorption of the metal. The procedure was repeated until complete combustion was achieved, which occurred when frothing stopped. Next, 10 mL of distilled water was added, the tube was manually shaken to loosen the soil and placed on a horizontal mechanical stirrer for an additional 3 min. Finally, the supernatant was combined with the previous extractors and filtered.

Amorphous Iron Oxide Fraction - AFeOx - 0.25 mol L^{-1} $NH_2OH.HCl$ + 0.25 mol L^{-1} HCl was used as an extractor, adjusted to pH 3.0 with concentrated NaOH, and added to the sample in the centrifuge tube. The tube was manually shaken and then placed on a horizontal mechanical stirrer for 30 min, centrifuged for 10 min, filtered and washed with 15 mL of distilled water. Next, it was manually shaken once again, submitted to mechanical stirring for a further 3 min, centrifuged, and the supernatant discarded.

Crystalline Iron Oxide Fraction - CFeOx - the extractor used was 0.2 mol L^{-1} $(NH_4)_2C_2O_4$ (ammonium oxalate) + 0.2 mol L^{-1} $H_2C_2O_2$ (oxalic acid) + 0.01 mol L^{-1} ascorbic acid, adjusted to pH 3.0 with concentrated NaOH. The extractor was added to the soil sample in the centrifuge tube, which was shaken manually, centrifuged, and then heated in a water bath at 100ºC for 30 min, with occasional stirring. Next, the samples were centrifuged for 10 min and the supernatant was filtered and placed in a capped flask.

Levels of Cd, Cu, Mn, Ni, Pb and Zn in the soil and water were determined by flame atomic absorption spectrometry (Perkin Elmer AAnalyst 800), with detection limits for Cd (0.002), Cu (0.005), Mn (0.05), Ni (0.002), Pb (0.003) and Zn (0.002). For quality control purposes, samples of multielement standard solutions (spikes) were used, prepared based on 1000 mg L^{-1} standards (TITRISOL®, Merck), with concentration equal to the central point of the calibration curve of the device.

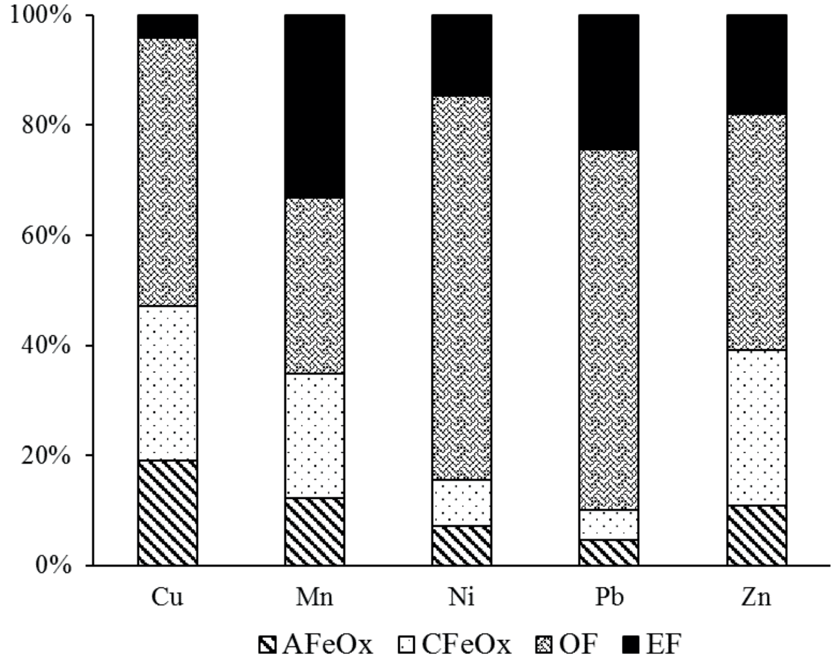
In order to understand the distribution of the fractionated metals associated with the exchangeable, organic matter, amorphous and crystalline iron oxide fractions under the influence of landscape positon, the results were analyzed by Tukey's test at 5% probability.

After standardization of variables with zero mean and unit variance ($\mu = 0$, $\sigma = 1$), the data were submitted to principal component analysis (PCA). The criteria adopted to select the number of components were those with eigenvalues above 1.00, as proposed by Kaiser (1958), and those capable of explaining cumulative variance above 70% (HAIR JUNIOR et al., 2009). All statistical analyses were processed using Statistica 7.0 software.

Results and Discussion

Figure 2 shows the fractions that most influenced heavy metal adsorption. The highest proportions of fractionated metals were found in the organic fraction (Figure 2), in the following descending order: Ni>Pb>Cu>Zn>Mn. The oxide fraction (*AFeOx* + *CFeOx*) contributed most to the retention of Mn, followed by Cu and Zn. The retention percentage for Mn among the fractions was the most similar (*OxFeA* + *OxFeC:* 35%, *FT*: 33% e *FO*: 32%), when compared to the other elements.

Figure 2. Percentage distribution of Cu, Ni, Mn, Pb and Zn in soil fractions cultivated with vegetables, at a depth of 0.00 - 0.20 m.



The effective participation of *OF*, which accounted for the largest portion of Ni, Pb, Cu and Zn in the soil cultivated with vegetables, can be explained by the formation of stable complexes between these metals and the carboxylic and phenolic radicals present in humic substances (fulvic and humic acids and humins) (BLUME; BRÜMMER, 1991; MELO et al., 2016; WU et al., 2017). Organic matter exhibits a pH-dependent charge, with predominantly negative charges in organic radicals at values greater than 3.5 (point of zero charge (PZC) of organic matter) due to the dissociation of H^+ ions and the formation of water, resulting in stable organometallic complexes (SPOSITO, 1989). This explains the effectiveness of organic matter in retaining heavy metals, since pH values in the farming areas were high, varying from 5.8 to 6.2 (Table 1). These pH values are the result of corrective practices such as liming, aimed at obtaining values close to alkalinity to improve soil chemical quality.

Soil texture ranging from sandy clay loam to sandy loam and sandy clay, according to the textural triangle, resulted in less contribution by the sand fraction in promoting the sand-metal complex (LINHARES et al., 2009). As such, organic matter largely dominates the adsorption of Ni, Pb, Cu and Zn under the present study conditions.

In turn, Cu was most associated with the *OF*, which plays an important role in the sorption of this element (VEGA et al., 2010). Organic matter tends to form insoluble complexes with Cu (SCHNITZER; KHAN, 1978), as well as soluble complexes that can migrate through the soil profile. The oxide fractions (*OxFeC* and *OxFeA)* also showed great affinity for the element. Studies have shown that Cu is preferentially adsorbed by specific binding with the mineral fraction associated with OM (CHAVES et al., 2009; ARENAS-LAGO et al., 2014), inhibiting the presence of Cu in the soil solution. The formation of these complexes explains the lower Cu content found in the *EF*, corroborating the results obtained by Nascimento and Fontes (2004) and Chaves et al. (2009). This is desirable from an environmental perspective due to the formation of more stable complexes in relation to those formed with organic matter alone.

However, it is important to note that the high Cu levels in the farming areas result from the extensive spraying of copper fungicide, such as the Bordeuax mixture widely used to control fungal diseases in tomato, chili pepper and lettuce crops. In vineyards in Rio Grande do Sul state, Casali et al. (2008) found approximately 25% of total bound to OM and identified successive copper pesticide applications as the main source of Cu in the soil.

In general, the heavy metal content in the native forest soil was always lower than that observed in the farming areas (Table 2). This reflects the low participation of these metals as constituents of the granite-gneiss rock that gave rise to the soil in question, as reported by Silva et al. (2016). Only Mn did not differ significantly between the cultivated and forest soils, due to its extensive natural and anthropogenic variation in the soil, ranging from 0.535 to 5.247 mg L^{-1} on average. According to Burt et al. (2003) and Biondi et al. (2011), the non-significant difference for Mn in natural and anthropic soils is due to the occurrence of more than one stage of oxygen reduction (Mn^{2+} and Mn^{3+}), depending on soil pH. A similar result was observed for Cu and Zn in the organic, amorphous and exchangeable fractions of the cultivated soil, regardless of landscape position and differing only when compared to the heavy metal content of forest soil.

Table 2. Average levels (mg L^{-1}) of Cu, Mn, Ni, Pb and Zn according to landscape positions and soil fractions in yellow latosol cultivated with vegetables and forest areas (reference), at a depth of 0.00 - 0.20 m.

Metal	Landscape Compartment	Fractions							
		Amorphous		Crystalline		Organic		Exchangeable	
Cu	Lower Slope	0.3584	Ba	0.5113	Bb	0.9700	Aa	0.0734	Ca
	Middle Slope	0.3504	Ca	0.5440	Bab	0.9730	Aa	0.0826	Da
	Upper Slope	0.3652	Ca	0.6676	Ba	1.1000	Aa	0.0758	Da
	Forest	0.2432	ABb	0.2300	Bc	0.3394	Ab	0.0498	Ca
Mn	Lower Slope	2.0136		2.9472		4.3484		5.2470	
	Middle Slope	1.0654		2.0220		2.5704		2.1730	
	Upper Slope	1.0200		1.8528		2.5152		3.2676	
	Forest	0.0810		0.8472		1.3824		0.5350	
Ni	Lower Slope	0.2192	Da	0.2800	Ca	2.0900	Aa	0.4422	Ba
	Middle Slope	0.2084	Da	0.2506	Cb	2.1282	Aa	0.4226	Ba
	Upper Slope	0.2084	Da	0.2512	Cb	2.1500	Aa	0.4298	Ba
	Forest	0.2168	Ca	0.2246	Cc	1.9786	Aa	0.4552	Ba

continue

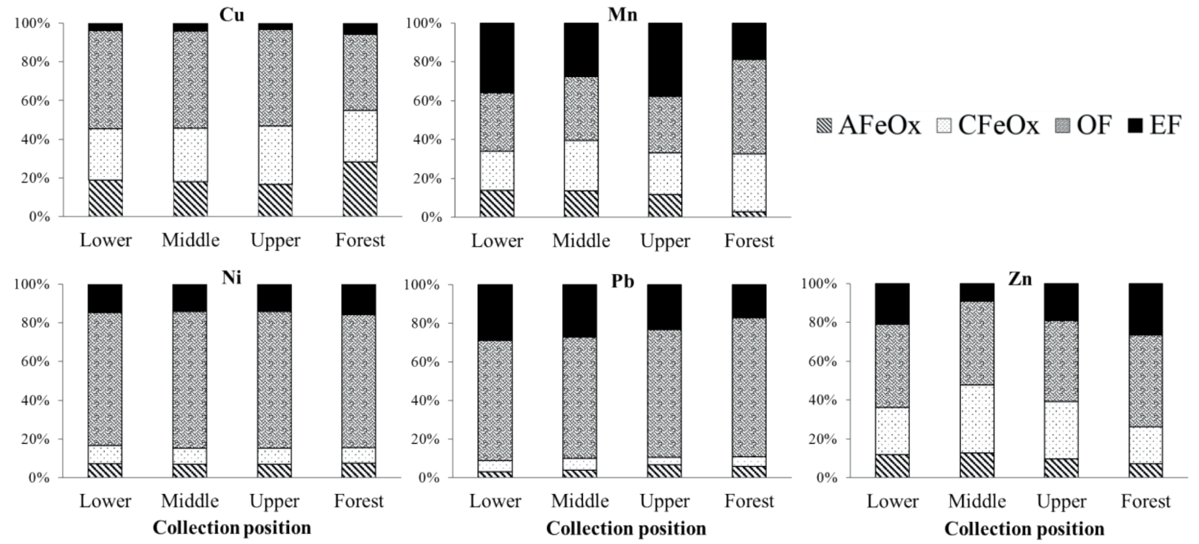
continuation

Pb	Lower Slope	0.1968	Ca	0.3800	Ca	4.0972	Aa	1.8994	Ba
	Middle Slope	0.2296	Ca	0.3776	Ca	3.7704	Aa	1.6528	Ba
	Upper Slope	0.4016	Ca	0.2314	Ca	3.9748	Aa	1.4180	Bab
	Forest	0.3468	Ca	0.3126	Ca	4.3588	Aa	1.0552	Bb
Zn	Lower Slope	0.2428	Ca	0.5008	Aa	0.8700	Aa	0.4324	Ba
	Middle Slope	0.2296	Ba	0.6228	Aa	0.7660	Aa	0.1660	Bb
	Upper Slope	0.2188	Da	0.6524	Ba	0.9288	Aa	0.4224	Ca
	Forest	0.0538	Cb	0.1390	BCb	0.3480	Ab	0.1966	Bb

[1] Means followed by the same letters (upper case in the rows and lower case in the columns) did not differ significantly according to Tukey's test at 5% probability.

The distribution of Pb among the three fractions was the same in both the cultivated and forest areas regardless of landscape position (Figure 3). Lead distribution for the different positions only varied significantly between the farming and forest areas in the exchangeable fraction (Table 2). The highest Pb levels were recorded in the organic fraction, with concentrations ranging from 3.77 to 4.36 mg L^{-1}. This means that although OM adsorbs a significant amount of Pb, it can easily be made available again by the soil, and that most adsorption sites show low affinity for the element. This interpretation is possible because *EF* levels varied from 1.05 to 1.9 mg L^{-1}, making it the second most important fraction in terms of Pb adsorption. Although several studies have found Fe, Al and Mn oxides to be the main adsorbers of Pb (SILVA; VITTI, 2008; LINHARES et al., 2009; KUMMER et al., 2011), this did not occur for the soil in question, likely because it is essentially kaolinitic, as characterized by Silva et al. (2001).

Figure 3. Percentage distribution of Cu, Ni, Mn, Pb and Zn in soil fractions cultivated with vegetables on the upper, middle and lower slope, at a depth of 0.00 - 0.20 m.



Although maintaining organic matter is important in the retention of Cu, Mn, Ni, Pb and Zn, this effect may not last due to weather conditions in the region, such as high rainfall and temperature, as well as intense soil mobilization (agricultural equipment and crop treatments), resulting in rapid organic matter degradation (KIRK et al., 2000). Additionally, organic matter acts as a physical barrier that prevents direct contact between the metal and the surface of the oxides (TAUJALE et al., 2016). This is the main cause of Ni and Pb transferring from the organic to the exchangeable fraction, due to the poor binding involved in this adsorption process. In the long term, and assuming intensive soil management, organic matter is rapidly degraded. This led to a significant increase in exchangeable Pb in soil from the farming and forest areas (Table 2), which is worrisome because lead is ranked second among hazardous elements and is a powerful carcinogenic agent (ATSDR, 2011).

For Zn, the *OF* and oxide fractions (*AFeOx* + *CFeOx)* were the most representative in terms of adsorption (Figure 3), with *CFeOx* significantly superior to *AFeOx* in all the landscape compartments (Table 2). Zinc is primarily present irreversibly in association with more stable soil components, such as crystalline and residual fractions (FERNÁNDEZ-CALVIÑO et al., 2012). However, in the present study organic matter played an important role in Zc retention, promoting the formation of less stable complexes (outer sphere), which in the short term may make the element available to the *EF* and, consequently, the vegetable crops.

Although landscape did not influence Zn distribution in the farming areas, since there was no significant difference (except for the *EF),* a statistical difference was observed between the fractions (Table 2). In soil, the oxide fractions are responsible for adsorbing most of the Zn (SILVA; VITTI, 2008), which is corroborated by our findings, given that around 43 % of Zn is associated with organic matter and 39% with *AFeOx* + *CFeOx*. The potential of organic matter to bind to Zn occurs because the rise in pH reduces Zn levels to the exchangeable form, concentrating the metal in the organic fraction (SHUMAN, 1986, 1998). Based on this explanation, the high soil pH (4.0 - 6.5) observed during the study, attributed to corrective chemical practices, increased the complexing capacity of Zn due to exposure to the predominantly negative net charge.

The high Mn concentrations, ranging from 3 to 5 mg L^{-1} in the *EF* of farming areas, indicate OM degradation resulting from soil turning practices, which led to an almost 50% in organic matter in relation to the farming areas. This inference can be interpreted by analyzing Mn levels in the forest soil, with concentrations of 0.5 mg L^{-1} in the *EF* (Table 2). The cycling process and conservative conditions in native vegetation environments, combined with the lack of anthropic activities, result in high soil OM content, meaning most Mn is retained in organic radicals, primarily fulvic acid. Additionally, as a natural polymer, OM forms organo-mineral complexes, justifying the second highest association of this metal with iron oxides (*AFeOx* + *CFeOx*).

Nachtigall et al. (2009) studied Mn availability using fractionation and found that a greater proportion of Mn bound to the organic (35%) and oxide fractions (30%) in soil samples at a depth of 0.0 - 0.10 m.

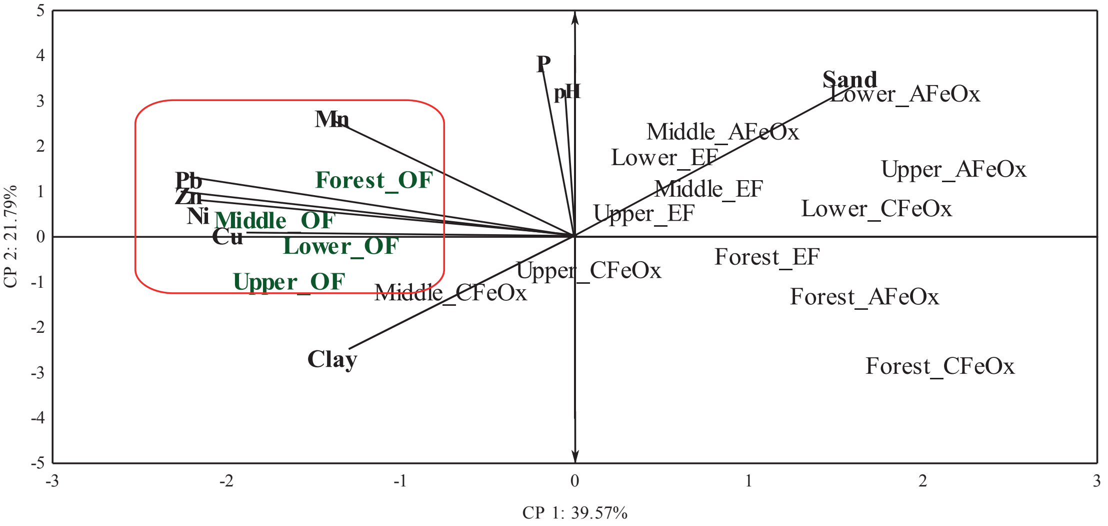
This is because the bonds between Mn and the oxide (*OxFeA* + *OxFeC)* and organic fractions (*OF*) vary from strong to covalent (inner sphere complex), weak or electrostatic (outer sphere complex), which is important in the short and long-term mitigation of serious environmental problems, as reported by Moreira et al. (2006, 2016).

The results obtained in principal component analysis (PCA) showed different patterns for cultivated soil in relation to soil from the forest areas (Figure 4). The total variance of the data retained in the first two principal components was 61.36% (39.57% in PC1 and 21.79% in PC2). PC1 was characterized by a process involving the organic fraction associated with Cu, Ni, Pb, Mn and Zn levels, contributing to a positive relationship. By contrast, PC2 involved the variables pH and P, which, given its location almost perpendicular to the axis, indicates a weak influence on the behavior of heavy metals.

In PC1, Cu, Ni, Mn, Pb and Zn fractionation is associated with organic matter and the clay fraction, which increases the adsorption site of the metals (OM + clay fraction). As such, it is important to underscore that even in sandy soils, organic matter is the decisive component in heavy metal complexation, since sand lacks charges that could interact with ionic species, as demonstrated in several studies (FREITAS et al., 2015; SILVA et al., 2016).

Furthermore, the soil under study was produced by the weathering of Precambrian granite and gneiss rock and, according to Correa et al. (2008), who studied the same soil type, contains low levels of iron oxides.

Figure 4. Principal component analysis of mean soil attributes at a depth of 0.00-0.20 m.



However, the present study showed a similar contribution by the oxide fraction and organic matter in Cu, Mn and Zn adsorption and identified these fractions as the main complexing agents, results that are consistent with those reported in similar studies (RAMALHO et al., 2000, FERNANDES et al., 2007; SILVA; VITTI, 2008).

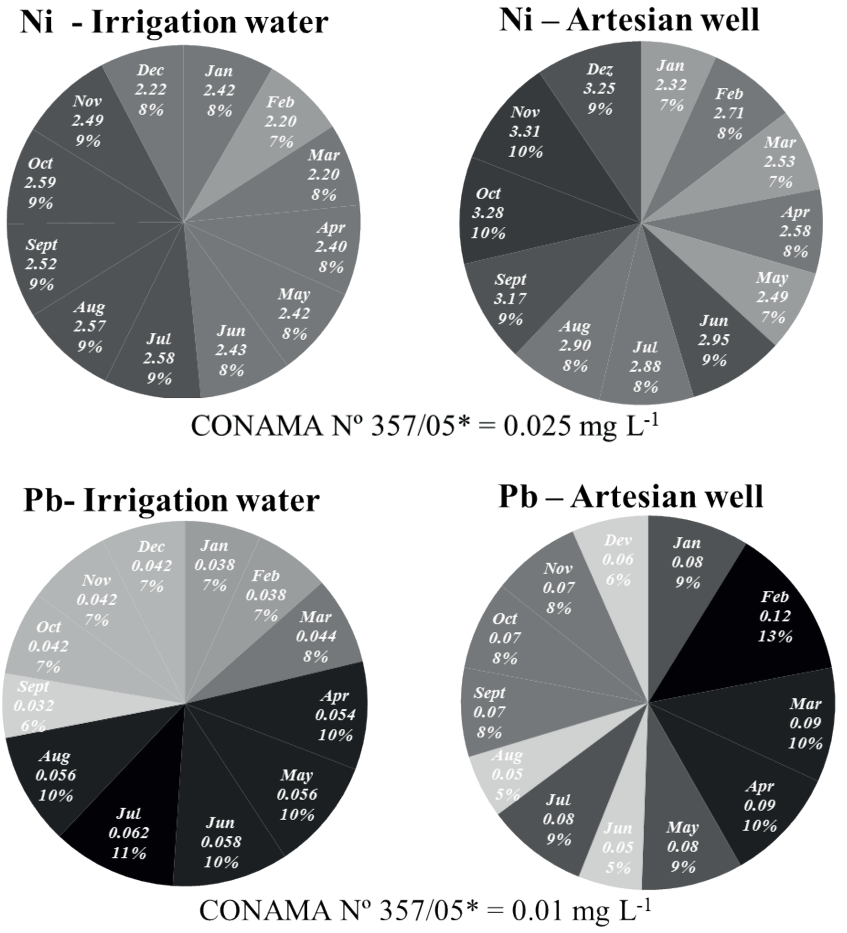
Nevertheless, the position of clay in PC2 correlates this fraction with *CFeOx*, assuming negative vectors, and reveals its secondary role in metal adsorption. With respect to landscape position, there was no clear distinction between the upper, middle and lower slope and the fractions associated with the metals, suggesting that position had little effect on the behavior of heavy metals in the fractions assessed. This information reiterates the findings presented in Table 2.

Only Ni and Pb were found in the water reservoirs used for crop irrigation and human consumption, (Figure 5). Levels of these elements were above those recommended by the legislation of 0.025 mg L^{-1} for Ni and 0.01 mg L^{-1} for Pb (CONAMA, 2005). The fact that Cu, Mn and Zn were not found in the water does not mean they were not present, but rather that they occurred in levels below the limit of detection (Cu = 0.005, Mn = 0.05, Ni = 0.002, and Zn = 0.002 mg L^{-1}) of the measuring device. This inference is reinforced by the total content reported by Silva et al. (2016) for this soil in Table 1.

Cu, Mn and Zn were not found in the water, which can be attributed to their low levels in the soil (Table 2) and association with the *AFeOx* and *CFeOx* fractions compared to Pb and Ni (Figure 2). The disturbed relief in the farming areas allowed OM to be carried by erosion, accumulating in the watercourses and raising the levels of adsorbed Pb and Ni in organic matter. These findings corroborate those obtained by Ramalho et al. (2000), who reported Ni and Pb levels above the legislative guidelines, resulting from excessive pesticide applications and the disturbed relief of the Caetés drainage basin in Rio de Janeiro state (RJ).

A temporal variation was observed for Ni and Pb in the reservoirs used for crop irrigation (Figure 2). Rainfall in the region varies, beginning in April and peaking in July, coinciding with the highest Pb concentrations of around 100% of total content. With respect to Ni, although levels tended to rise at the onset of the rainy season, the increase was less than that recorded for Pb. This may be because only 10% of Pb was associated with *AFeOx* and *CFeOx* fractions compared to 15.5% of Ni, making Pb more mobile in the soil (Figure 2). Magalhães et al. (2016) also found high Pb levels, among other metals, in river water in Pantanal Norte, Mato Grosso state (MT), Brazil. The results indicate loss of these metals adsorbed to soil and organic matter via erosion and their concentration in waterways, corroborating other studies using the same approach (RAMALHO et al., 2000; MAGALHÃES et al., 2016).

Figure 5. Heavy metals in water samples from five reservoirs and an artesian well used to irrigate vegetable crops and for human and animal consumption in the municipality of Camocim de São Félix, Pernambuco state.



In light of the findings, we can confirm that although the water analyzed was from the same source, contamination in the irrigation water did not reach the subsurface water of the artesian wells. However, it is still too soon for more robust long-term conclusions based on these results. As such, further research is needed to monitor and identify contaminant sources. This will allow for immediate intervention in the form of conservation practices aimed at reducing soil and organic matter losses and decreasing the excessive application of chemical inputs, in addition to phytoremediation practice such as using resistant plants to extract and accumulate heavy metals in contaminated soil (JADIA; FULEKAR, 2009; ANDRADE et al., 2009a).

Conclusions

Landscape position only interfered significantly in heavy metal adsorption in the soil for Cu and Ni associated with *CFeOx* and Zn bound to the *EF* in the farming areas.

The highest Cu, Ni, Pb and Zn levels were found in the fractions with less stable chemical bonds (bound to organic matter), in addition to a strong affinity between Cu, Zn and Mn and the oxide fractions (*AFeOx* + *CFeOx)*.

The low affinity of Pb and Ni for the *AFeOx* + *CFeOx* fractions indicates greater contamination potential for the water reservoirs.

In the short term, organic matter is the main source of remediation for heavy metal contamination in soil, making it important to adopt conservation practices aimed at reducing OM losses.

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