Heavy metal contents in Latosols cultivated with vegetable crops[1]

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ABSTRACT

Heavy metals are naturally found in soils, but their levels may increase as a result of anthropogenic actions. This study aimed at determining the concentrations of Cd, Cu, Mn, Ni, Pb and Zn in Yellow Latosol from vegetable crops areas, as well as the influence of the cultivation and position in the landscape on the accumulation of these elements. Soil samples were collected from five farming areas and four areas with natural vegetation, which served as a reference. Soil was collected along the planting rows from three transect positions (upper, middle and lower sections of the slope), as well as from the upper portion of forest areas, at three depths (0.0-0.10 m, 0.10-0.30 m and 0.30-0.60 m). The results from the chemical analyses indicated that Cd, Cu, Mn, Pb and Zn levels in the soil increased as a result of cultivation. Only Cd and Cu concentrations were above the quality reference values for the Pernambuco State. The multivariate analysis techniques used were efficient at separating the environments and at differentiating the origin of the metals. Soils from forest areas were clearly separated from croplands, demonstrating the effect of agricultural practices on the metal contents in the soils. The principal component analysis indicated a predominantly anthropogenic origin (phosphate fertilizing) for Cd, in more superficial soil samples.

KEYWORDS: Trace metals; multivariate analysis; cadmium.

RESUMO

Teores de metais pesados em Latossolos cultivados com olerícolas

Metais pesados são naturalmente encontrados em solos, mas suas concentrações podem ser aumentadas por meio de ações antrópicas. Objetivou-se determinar as concentrações de Cd, Cu, Mn, Ni, Pb e Zn em Latossolos Amarelos de áreas produtoras de olerícolas, bem como a influência do cultivo e da posição no relevo dos solos no acúmulo desses elementos. Amostras de solo foram coletadas em cinco propriedades e quatro áreas com vegetação natural, as quais serviram de referência. O solo foi coletado nos terços superior, médio e inferior da encosta, nas linhas de plantio, e no topo, nas áreas de mata, em três profundidades (0,0-0,10 m; 0,10-0,30 m; e 0,30-0,60 m). Os resultados das análises químicas demonstraram que as concentrações de Cd, Cu, Mn, Pb e Zn nos solos foram aumentadas pelo cultivo. Apenas Cd e Cu estiveram acima do valor de referência de qualidade para Pernambuco. As técnicas de análise multivariada utilizadas foram eficientes para separação dos ambientes e para diferenciação da origem dos metais. Os solos nas áreas de mata foram claramente separados das áreas de cultivo, demonstrando o efeito das práticas agrícolas sobre os teores dos metais nos solos. A análise de componentes principais indicou origem predominantemente antropogênica (adubação fosfatada) para Cd, nas amostras de solo mais superficiais.

PALAVRAS-CHAVE: Metais-traço; análise multivariada; cádmio.

INTRODUCTION

The use of agrochemicals has become a common practice for maintaining high yields and controlling pests and diseases that compromise the productive potential of crops. These practices may lead to soil contamination, due to the accumulation of potentially toxic elements or compounds, such as heavy metals.

Increased heavy metal contents in the soil may interfere with crop growth, quantitatively and qualitatively compromising food security. Food chain contamination may harm human health and ecosystems (Lee et al. 2006, Luo et al. 2007, Freitas et al. 2009).

Heavy metals are naturally present in soils and their levels are dependent on the material that originated the soil and the degree of soil development.

Under normal conditions, heavy metals are not found in soils at concentrations that represent a risk to the environment or human health. On the other hand, activities such as mining, waste disposal, atmospheric deposition and intense farming activity may increase heavy metal contents in the soil (Mendes et al. 2006 and 2010, Peris et al. 2007).

Secondary constituents of mineral fertilizers containing phosphate, derived primarily from phosphate rocks, include heavy metals, most notably Cd, Cu and Zn, which are not eliminated in the manufacturing process and accumulate in the soil through successive applications (Agbenin 2002). As such, phosphate fertilizer has been considered an important source of heavy metal contamination in many parts of the world (Micó et al. 2006, Sun et al. 2013, Kelepertzis 2014). Increased Cd content due to phosphate fertilizer in muskmelon crops was reported by Mendes et al. (2006). Freitas et al. (2009) assessed the availability of Cd and Pb in phosphate-fertilized soil and observed increased levels proportional to the doses applied in the soil and in maize plants.

Knowing the origin of heavy metals in the soil is essential to assess their possible impact on the environment and to propose alternatives to the contamination source. Statistical techniques, such as multivariate analysis, may be useful in separating areas and interpreting environmental data, since they help to distinguish between natural contributions of metals in the soil and those from anthropogenic sources (Micó et al. 2006, Naveedullah et al. 2013, Sun et al. 2013, Parelho et al. 2014). This differentiation is important to establish quality reference values for metals in the soil and for assessing the risk of crop or groundwater contamination in agricultural areas.

Olericulture, characterized by intensive soil management over small areas of land, is one of the agricultural activities that use the largest amount of agrochemicals. As such, monitoring the soil quality in these areas is vital for risk assessment. For example, Peris et al. (2007) recorded Cu, Pb and Zn enrichment in soil used to grow vegetables in Spain, while Alam et al. (2003) reported the contamination of vegetable species with As, Cd and Pb, in a soil in Bangladesh.

The present study aimed at determining the concentrations of Cd, Cu, Mn, Ni, Pb and Zn in Yellow Latosols under vegetable crops and natural vegetation formed at different positions in the landscape.

MATERIAL AND METHODS

The study was conducted in farming areas of Camocim de São Félix, Pernambuco State, Brazil, in 2011, where the predominant climate is As (rainy tropical climate with dry summer), according to the Köppen-Geiger classification system. The average annual temperature is around 24 ºC, ranging 20-22 ºC in the coldest months and 22-33 ºC in the warmest months, with annual rainfall of 900-1,300 mm. Altitudes exceed 600 m, but rarely surpass 1,000 m, with an undulated to sharply undulated relief. The soils in the region are highly to moderately developed. The natural vegetation consists primarily of deciduous and/or semi-deciduous forests (Vieira 2011).

Based on site visits and information from the local branch of the Instituto Agronômico de Pernambuco and rural farmers, five farming areas (A1, A2, A3, A4 and A5) with a typical management system for the region and four forest areas (F1, F2, F3 and F4) from fragments of secondary forest vegetation at the top of the slope, which served as local reference areas, were selected. The areas were georeferenced using a Garmin GPS device and eTrex Vista HCx (Table 1).

The soil in the different sampling sites is classified as Yellow Latosol (Embrapa 2013). This soil is equivalent to the Xanthic Ferralsol (FAO 1990). With respect to geology, according to Brasil (1973), the soil developed from Precambrian rocks consists of gneisses and granites, with sandy clay material on the surface of some soils (Table 1). As highlighted by Silva et al. (2001), Yellow Latosols occupy the top and upper segments of slopes in the studied areas. Textural differences are due to the possible occurrence of the soil in a transition zone between the two geological materials and their position in the landscape.

In the cultivated areas, soil samples were collected along the planting rows, totaling 10 simple samples for every compound sample in each transect position (upper section - U; middle or slope - S; and lower section - L), at 3 depths (0.0-0.10 m, 0.10-0.30 m and 0.30-0.60 m). Thus, the areas were divided into the following segments: A1 = U1, S1, L1; A2 = U2, S2, L2; A3 = U3, S3, L3; A4 = U4, S4, L4; and A5 = U5, S5, L5. In the forest areas (F), sampling was performed in a zigzag pattern along the upper section, at the same three depths, with 10 simple samples comprising one compound sample.

Samples were air dried (air-dried fine earth), broken up and sieved in a 2.00 mm mesh nylon sieve.

Latosol samples were chemically characterized (Table 2) in accordance with Embrapa (2011), as it follows: pH: H_2O; Ca^{2+} and Mg^{2+}: extracted using 1 mol L^{-1} of a potassium chloride solution and analyzed by titration with EDTA at 0.0125 mol L^{-1}; $H^+ + Al^{3+}$: extracted using 1 mol L^{-1} of a calcium acetate solution at pH 7.0 and determined by titration with NaOH 0.0606 mol L^{-1}; available P^- and K^+: extracted with a Mehlich-1 solution, where P was measured by colorimetry and K^+ by atomic emission spectroscopy; organic carbon: obtained by the Walkley-Black method. The data obtained were used to calculate the sum of base cations, cation exchange capacity, base saturation (%) and aluminum saturation (%).

For physical characterization, soil samples were collected at depths of 0.0-0.30 m and 0.30-0.60 m, for particle size analysis, using the pipette method and 0.1 mol L^{-1} of NaOH (Ruiz 2005). The clay fraction was separated by sedimentation, total sand by sieving, and silt was calculated based on the difference between them. Soil texture was classified based on the proportions of sand, silt and clay, using the USDA soil texture triangle (USA) (Table 1).

In order to determine Cu, Mn, Ni, Pb and Zn contents, a 5 cm^3 aliquot of soil was ground using an agate mortar and pestle and sieved in a 0.3 mm mesh stainless steel sieve (ABNT n. 50) to prevent contamination. Soils samples were digested using the USEPA 3051A method (USEPA 1998). Samples of 1 g were placed in Teflon tubes added with 9 mL of HNO_3 and 3 mL of HCl (p.a.). The tubes were maintained in a closed system consisting of a microwave oven (Mars Xpress) at a 8'40'' temperature ramp, the time required to reach 175 ºC, which was sustained for another 4'30''. After cooling, the samples were transferred to certified 25 mL volumetric flasks (NBR ISO/IEC), which were topped up with distilled water, and the extracts immediately filtered through qualitative filter paper (Macherey Nagel®).

Digestion and determination were performed in triplicates, with the first two runs used in calculations and the third in the event of dissimilarity between the values obtained. The Cd, Cu, Mn, Ni, Pb and Zn contents of the extracts were determined by flame atomic emission spectrometry (AAnalyst 800 Perkin Elmer). The limits of quantification for the equipment were 0.002, 0.005, 0.05, 0.002, 0.003 and 0.002, respectively for Cd, Cu, Mn, Ni, Pb and Zn. For the quality control of the analysis, a recalibration curve and determination of the metal concentration in spikes samples prepared with analytical standards, whose recoveries ranged 88-102 %, were used.

Table 1. Altitude, geographic coordinate, classification and textural class of the Yellow Latosols studied.

Area	Coordinate	Altitude	Depth	Sand	Silt	Clay	Textural class
			m ————	———— g kg^{-1} ————			
A1	8º22'38.5''S and 35º45'56.9''W	672	0.00-0.30	560	160	280	Sandy clay loam
			0.30-0.60	610	100	290	
A2	8º22'40.9''S and 35º45'58.2''W	673	0.00-0.30	420	60	520	Sandy clay loam
			0.30-0.60	540	240	220	
A3	8º20'32.6''S and 35º45'02.1''W	674	0.00-0.30	580	60	360	Sandy loam
			0.30-0.60	500	80	420	
A4	8º20'33.7''S and 35º45'06.1''W	675	0.00-0.30	730	60	210	Sandy clay
			0.30-0.60	560	170	270	
A5	8º20'46.3''S and 35º44'49.9''W	688	0.00-0.30	540	120	340	Sandy clay loam
			0.30-0.60	730	100	170	
F1	8º21'17.0''S and 35º44'46.7''W	691	0.00-0.30	370	60	570	Sandy clay
			0.30-0.60	450	160	390	
F2	8º21'05.2''S and 35º44'40.9''W	701	0.00-0.30	610	80	310	Sandy clay loam
			0.30-0.60	570	120	310	
F3	8º20'41.6''S and 35º44'46.9''W	688	0.00-0.30	570	210	220	Sandy clay loam
			0.30-0.60	550	120	330	
F4	8º20'11.6''S and 35º44'46.6''W	709	0.00-0.30	600	190	210	Sandy clay loam
			0.30-0.60	540	90	370	

A1 = area 1; A2 = area 2; A3 = area 3; A4 = area 4; A5 = area 5; F1 = forest 1; F2 = forest 2; F3 = forest 3; F4 = forest 4.

Management techniques were similar for all areas, regardless of the land relief or crop, with consecutive vegetable crops along the transect, use of irrigation, preventive and corrective application of fertilizers and pesticides. The slope was similar in all areas (A1 = 31 %; A2 = 33 %; A3 = 32 %; A4 = 33 %; and A5 = 32 %). Planting was carried out in short, closed level furrows and medium-sized holes, where seeds and/or seedlings, as well as fertilizers, were placed. Mineral and organic fertilizers and pesticides were used in a generalized manner, without technical criteria or agricultural guidance. Farmers were interviewed regarding fertilizer and pesticide application, as well as crops grown in the previous five years.

In addition to other chemical products, common mineral fertilizers used for vegetable crops include monoammonium phosphate, diammonium phosphate, single superphosphate, urea, NPK formulations (06-24-12; 20-10-20; 10-10-10; 10-20-20; and 20-0-20), potassium chloride, potassium sulfate, micronutrients (FTE), foliar fertilizers (Zn), ammonium sulfate, calcium nitrate and potassium nitrate.

The herbicides and pesticides used include Chess 500 WE, Lannate BR, Malathion 100 EC, Fastac 100, Haiten, Sumidan 25 EC, Ajifol, Manzate WG, Roundup, Polytrin, Quimifol, Trigard 750 WP, Bravonil Utrex, Cercobim 500 SC, Priori Xtra, Score, Cabrio Top, Folicur 200 EC, 22 Captan SC, Cuprozeb, Sumilex, Derosal Plus, Maxin XL,

Table 2. Chemical characteristics of soils in the farming (A1, A2, A3, A4 and A5) and forest (F1, F2, F3 and F4) areas.

Chemical attribute	Unit	A1			A2			A3			A4			A5			F1	F2	F3	F4
		U1	S1	L1	U2	S2	L2	U3	S3	L3	U4	S4	L4	U5	S5	L5	U1	U2	U3	U4
								0.0-0.10 m depth												
pH	H_2O	6.1	6.4	6.2	5.2	6.5	6.1	5.7	5.9	5.2	5.6	6.2	5.2	6.5	6.2	6.5	4.8	4.6	4.6	4.2
Ca	$cmol_c\ dm^{-3}$	5.7	5.0	4.1	3.2	4.0	4.5	3.7	3.2	2.6	4.8	4.1	3.3	4.0	5.0	4.5	1.5	1.3	1.0	0.8
Mg	$cmol_c\ dm^{-3}$	1.4	2.2	2.5	2.6	2.7	1.6	1.5	0.8	1.1	2.5	2.3	1.5	3.6	2.9	0.8	3.2	1.5	2.7	3.0
P	$mg\ dm^{-3}$	172	162	275	275	279	58	109	166	137	149	380	246	146	44	36	8.0	6.0	8.0	5.0
K	$cmol_c\ dm^{-3}$	1.8	1.4	1.6	1.0	2.6	0.1	0.3	0.2	1.0	2.0	2.5	1.6	2.5	2.4	0.9	0.5	0.1	0.2	0.2
OM	$g\ kg^{-1}$	25.5	25.2	17.8	32.4	23.6	30.3	17.1	13.0	14.8	28.1	24.2	19.1	27.5	24.4	18.9	45.5	43.2	38.6	39.7
H + Al	$cmol_c\ dm^{-3}$	2.15	2.15	1.98	5.61	2.64	3.63	3.80	2.15	2.48	4.62	1.16	1.82	1.82	0.83	2.15	13.53	12.38	5.28	11.39
CEC	$cmol_c\ dm^{-3}$	11.12	10.85	10.28	12.52	12.24	10.17	9.46	6.49	7.23	14.12	10.23	8.27	11.96	11.24	8.31	18.81	15.29	9.37	15.40
m	%	1.35	0.92	0.97	0.80	1.23	0.98	1.06	1.54	0.69	1.77	0.98	121	0.84	0.89	0.60	4.25	7.19	7.47	6.17
V	%	80.71	80.23	80.74	55.17	78.44	64.29	59.86	66.93	65.79	67.28	88.71	78.04	82.84	92.66	74.20	28.05	19.09	43.65	26.05
								0.10-0.30 m depth												
pH	H_2O	6.2	6.6	6.4	5.5	6.4	5.9	6.1	5.7	5.4	5.5	6.6	5.4	6.8	6.4	5.4	4.5	4.6	4.5	4.4
Ca	$cmol_c\ dm^{-3}$	5.4	4.7	4.0	2.7	3.3	4.3	3.2	3.1	2.8	4.0	3.6	2.8	3.6	4.1	3.7	1.3	1.2	1.1	0.6
Mg	$cmol_c\ dm^{-3}$	1.5	3.0	2.1	2.6	3.1	2.9	0.7	0.6	1.2	1.9	1.9	1.4	3.1	0.9	0.4	1.5	2.5	1.6	1.7
P	$mg\ dm^{-3}$	139	120	287	107	62	45	136	203	132	85	435	176	36	51	20	5.0	4.0	3.0	4.0
K	$cmol_c\ dm^{-3}$	1.3	0.8	1.3	1.7	0.7	0.1	0.1	0.1	0.5	0.5	0.6	0.6	1.7	1.1	0.2	0.6	0.1	0.1	0.1
OM	$g\ kg^{-1}$	15.8	20.6	19.0	26.1	15.5	19.1	11.9	9.6	11.0	21.1	14.3	12.0	22.5	21.8	24.2	43.2	38.6	32.6	33.4
H + Al	$cmol_c\ dm^{-3}$	1.98	1.98	2.31	5.28	2.31	3.14	1.98	1.98	2.15	4.79	1.16	1.16	2.81	1.65	3.63	14.36	11.88	7.26	8.58
CEC	$cmol_c\ dm^{-3}$	10.20	10.57	9.70	12.50	9.59	10.55	6.10	5.82	6.68	11.25	7.30	6.12	11.33	7.79	7.98	17.87	15.79	10.11	11.03
m	%	1.47	0.95	1.03	0.80	3.13	0.95	1.64	1.72	0.75	2.22	1.37	1.63	1.32	1.28	1.88	7.28	7.28	9.49	13.15
V	%	80.59	81.26	76.18	55.77	75.90	70.27	67.51	66.00	67.90	57.47	84.17	81.14	75.24	78.82	54.49	19.66	24.76	27.49	22.18
								0.30-0.60 m depth												
pH	H_2O	6.3	6.9	6.4	5.3	6.6	6.8	5.5	5.6	6.5	6.1	6.5	5.9	6.4	6.3	5.1	4.8	4.7	4.3	5.2
Ca	$cmol_c\ dm^{-3}$	5.6	5.7	3.3	2.6	3.3	3.7	2.5	2.4	2.6	4.4	3.5	2.1	2.2	3.5	1.8	1.4	1.2	1.3	0.5
Mg	$cmol_c\ dm^{-3}$	1.6	1.5	1.7	1.5	2.0	0.9	0.7	0.9	0.4	1.2	0.9	1.1	1.9	1.9	0.9	1.5	2.7	1.0	1.4
P	$mg\ dm^{-3}$	171	185	389	115	35	65	112	112	73	84	340	138	13	14	8.0	6.0	2.0	2.0	2.0
K	$cmol_c\ dm^{-3}$	1.2	0.9	0.6	2.1	0.5	0.0	0.1	0.2	0.3	0.9	0.5	1.6	2.6	0.9	0.1	0.7	0.1	0.1	0.1
OM	$g\ kg^{-1}$	17.5	15.8	15.9	16.9	14.8	12.0	7.3	5.5	5.5	19.0	8.5	8.0	20.5	22.2	16.0	37.1	35.7	21.9	27.8
H+Al	$cmol_c\ dm^{-3}$	1.82	1.65	1.82	6.27	3.96	1.65	1.65	1.82	1.16	4.62	0.66	0.83	4.46	3.47	5.45	13.20	11.06	8.75	7.26
CEC	$cmol_c\ dm^{-3}$	10.37	9.92	7.43	12.68	9.93	6.49	5.05	5.35	4.50	11.16	5.69	5.83	11.29	9.76	8.29	16.79	15.15	11.07	9.23
m	%	0.48	1.01	3.37	1.58	1.51	1.54	1.98	0.93	1.11	0.45	1.76	0.86	1.77	2.05	8.44	7.74	7.59	12.64	20.05
V	%	82.50	83.37	75.56	50.54	60.10	74.59	67.30	66.09	74.35	58.61	88.39	85.82	60.54	64.51	34.34	21.37	27.01	21.02	21.31

A1 = area 1; A2 = area 2; A3 = area 3; A4 = area 4; A5 = area 5; F1 = forest 1; F2 = forest 2; F3 = forest 3; F4 = forest 4; U1 = upper 1; U2 = upper 2; U3 = upper 3; U4 = upper 4; U5 = upper 5; S1 = slope 1; S2 = slope 2; S3 = slope 3; S4 = slope 4; S5 = slope 5; L1 = lower 1; L2 = lower 2; L3 = lower 3; L4 = lower 4; L5 = lower 5.

Amistar WG, Actara, Karate Zeon 250 CS, Pirate, Decis 25 EC, LoSBan 480, Furadan 350 TS, Dimilin, Marshal 400 SC, Dual Gold, Topik 240 EC, Fusilate 250 EW, Cobra, Roundup Ultra, Goal BR, Diuron, Acephate and Methamidophos.

Historically, the crops cultivated in the studied areas were tomato, cabbage, chard, lettuce, bell pepper, eggplant, maize, São Tomé yam, zucchini, cauliflower, cilantro, chive, leek, basil, green bean, chayote, cowpea, medicinal herbs, passion fruit, carrot, strawberry, papaya and ornamental species.

Data were submitted to analysis of variance and means compared by the Tukey test (p = 0.05). Then, multivariate statistical analysis was applied. After standardization of the variables (P, organic matter and heavy metals) to zero mean and unit variance, data were submitted to cluster analysis and principal component analysis. The cluster analysis was composed only by the variables heavy metals, crop areas, depths and landscape segments, while the principal component analysis involved, besides these variables, P and organic matter.

Hierarchical clustering was performed using the Euclidean distance as the similarity measure and the Ward's method as a clustering strategy (Hair et al. 2005). Results were presented in graphic form (dendrogram), facilitating the identification of clusters.

Principal component analysis was conducted to obtain a smaller set of linear combinations of variables that preserved most of the information provided by the original variables (Silva et al. 2010). The criteria adopted to select the number of components were those with eigenvalues above 1.00 (Kaiser 1958), and capable of explaining cumulative variance above 70% (Hair et al. 2005). All statistical analyses were processed using the Statistica 7.0 software.

RESULTS AND DISCUSSION

Except for Ni, heavy metal contents in the soil were higher in cultivated areas than those with natural vegetation, and were influenced by the position of the transect and depth (Figure 1).

The soil Ni status is highly dependent on its levels in the parent material and anthropogenic additions. As such, Ni content at the surface reflects both soil contamination and formation processes (Kabata-Pendias & Pendias 2001).
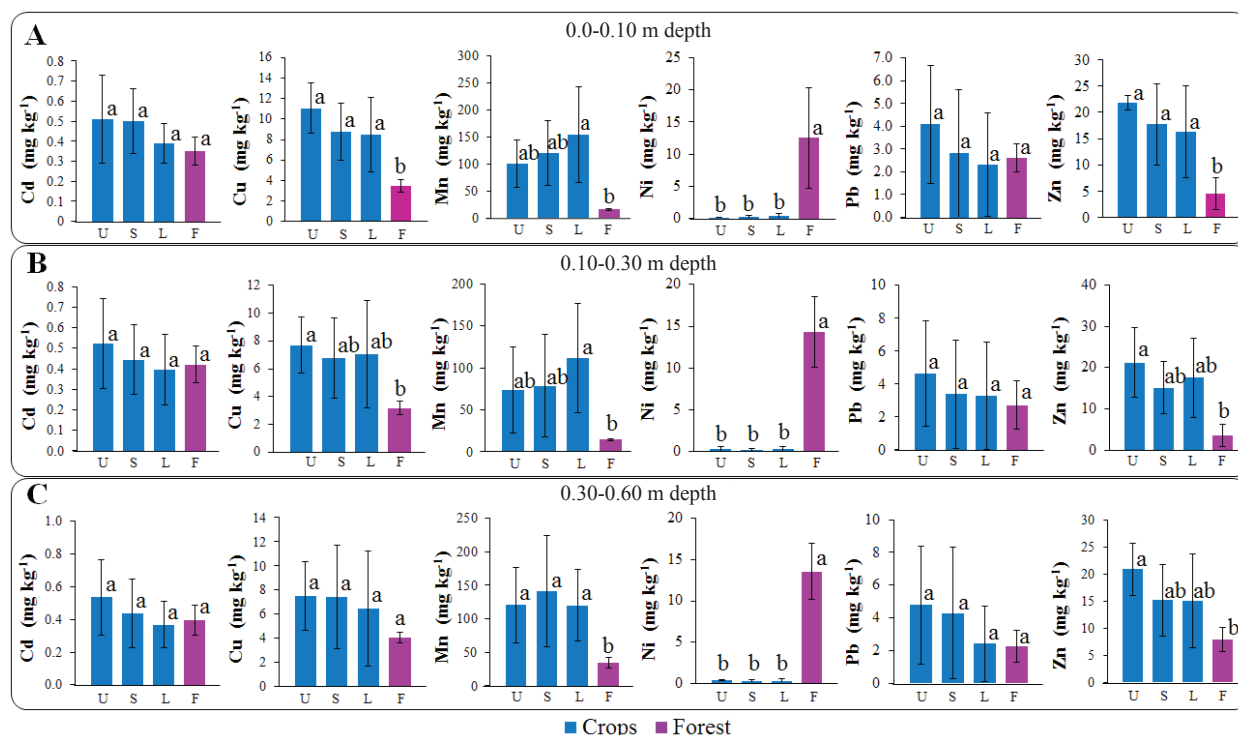

Figure 1. Total heavy metal content in Yellow Latosols used for vegetable crops and natural vegetation. F = forest areas. Crop areas: U = upper; S = slope; L = lower. Means followed by the same letter do not differ significantly (p < 0.05) by the Tukey test.

Nickel concentrations in the soil varied from zero to 18.6 mg kg^{-1} (Figure 1). Considering that the quality reference values for Ni in soils of the Pernambuco State is 9 mg kg^{-1} (Pernambuco 2014), levels of this element were higher than the quality reference values in 17 soil samples studied. However, it is important to note that no levels exceeded the prevention value of 30 mg kg^{-1} established by Conama (2009), above which monitoring of likely contamination is recommended. Moreover, the fact that the Ni content was always higher in forest areas than in cultivated soil reinforces the natural origin of the element.

Decreased Ni levels may occur in cultivated areas due to Ni removal by crops, uptake via agricultural inputs or leaching into deeper soil layers (Mendes et al. 2006, Antoniadis & Tsadilas 2007). In addition, Ni exhibits greater affinity to soil organic matter (Senesi et al. 1989), which is found in higher concentrations in soils under natural vegetation (Table 2), and may reduce Ni losses in the system.

Despite Cd, Cu, Mn, Pb and Zn enrichment in the soil, as a result of crops, only Cd and Cu were above the quality reference values (0.5 mg kg^{-1} and 5 mg kg^{-1}, respectively) for the Pernambuco State (Pernambuco 2014). Nevertheless, levels of both elements were below the prevention value (1.3 mg kg^{-1} and 60 mg kg^{-1}, respectively) stipulated by Conama (2009).

Cadmium is one of the most worrisome metals, in terms of soil quality, and may be influenced by the addition of agricultural inputs. Even at low concentrations, its toxicological effects on living organisms are greater than those caused by high levels of other metals. However, the Cd content in this study was below or close to the quality reference values (Figure 1), indicating only minor uptake via non-natural sources. Only in the upper section of the cultivated areas, regardless of depth, the Cd levels were slightly higher than the quality reference value, which is 0.5 mg kg^{-1} (Pernambuco 2014). In the upper section, the Cd enrichment in the soil generally results from fertilizers, particularly phosphate fertilizers (Mendes et al. 2006, Freitas et al. 2009).

In general, the Cu content was significantly higher in the cultivated soil. Increased soil Cu levels are associated with the use of different fungicides, especially Cu-based pesticides (Mirlean et al. 2007, Komárek et al. 2008). Fungicides were routinely applied to vegetable crops and the practice was reported by farmers in the study areas.

The behavior of Zn was similar to Cu, i. e., there was a slight increase in its levels in the cultivated soil. Soil Zn content reached a maximum of 9.4 mg kg^{-1} in areas with natural vegetation and 36.1 mg kg^{-1} in cultivated areas (Figure 1). The rise in total Zn content in cultivated areas, if compared to forest areas, implies an anthropogenic influence on the addition of this metal to the soil. Zinc levels in the soil may rise by 0.5-1.0 mg kg^{-1} year^{-1}, due to the use of fungicides and fertilizers containing this element (Weingerl & Kerin 2000). The high P content recorded (Table 2) owing to the use of phosphate fertilizers may also be responsible for the increase in Zn, with cultivation.

Despite the significant increase in the Pb content in cultivated soils, all the levels measured were below the quality reference value for the Pernambuco State, which is 13 mg kg^{-1} (Pernambuco 2014). These low levels may be due to the lack of minerals containing lead in the parent material (Wuana & Okieimen 2011). Thus, Pb quantified in soils under cultivated and forest areas comes from the crystalline structure of aluminosilicates, what suggests a sole contribution by the parent material. In this case, as reported by Pereira & Kawamoto (2009), the Pb levels found may be considered a natural effect of the geochemistry in the region, i.e., the Pb content depends solely on the weathering of rocks, with no apparent contaminants present.

The highest Mn levels were recorded in the cultivated areas (Figure 1). The significant increase in the total Mn content in these areas may be due to the management practices adopted for vegetable growing. Levels of a metal added to the soil through waste disposal, agrochemical or atmospheric deposition will rise if it is not removed from the environment through leaching or by crops (Revoredo & Melo 2006). In the cultivated areas, particularly at the first two depths, Mn levels were very high, in relation to areas under natural vegetation, what corroborates the inflow of the element via agricultural inputs.

Hierarchical clustering was performed, obtaining a significant variation in Euclidean distances for the set of variables considered, enabling the division of groups (Figure 2). A grouping threshold was established at a distance of 5 (for the three depths studied), indicating the formation of three clusters.

Cluster 1 (CI) consisted of the areas F1, F2, F3, F4 and A5 (for the slope and lower section - S5

and L5, respectively), which were characterized by low Cu and Zn levels (but high Ni content) and low Mn concentrations at the depths of 0.10-0.30 m and 0.30-0.60 m. The low Cu, Mn and Zn values in these environments may be due to the lack of anthropogenic interference in the forest areas studied, while high Ni levels may be the result of losses through cultivation and greater conservation of the element in the forest organic matter.

Cluster 2 (CII) comprised L4, L3, S3 and U3 in the surface layer (0.0-0.1 m). At the remaining depths, in addition to the environments L4, L3, S3 and U3, the slope environment S4 was also present, due to undetected Pb in areas A3 (U, S, L) and A4 (S, L) (Figures 1 and 2). The soil samples L1, L2, U1, U2, U4, U5, S1, S2 and S4 were grouped into Cluster 3 (CIII) owing to the high Cd levels recorded, closer to those in the remaining segments. In the Rio de Janeiro State, Ramalho et al. (2000) also found a significant increase in the Cd content in vegetable growing areas where pesticides and phosphate fertilizers were consistently applied.

At depths of 0.0-0.10 m and 0.10-0.30 m in CI, the formation of a subgroup contained L5 and S5 isolated from the forest areas (Figures 2a and 2b), due to the natural condition of the vegetation. Additionally, segments L5 and S5 exhibited high Mn and Pb levels and low organic matter content, what suggests the anthropogenic entry of these metals into the system.

The hierarchical clustering analysis made it possible to visualize the separation of the areas, which were clustered into homogeneous groups based on the degree of similarity. Principal component analysis was also used to identify the variables with the greatest discriminatory potential for each area (Table 3). Eigenvectors may be considered measures of the relative importance of each variable in relation to the principal components, with positive or negative signs indicating directly or inversely proportional relationships, respectively. As such, the variables that best explain or
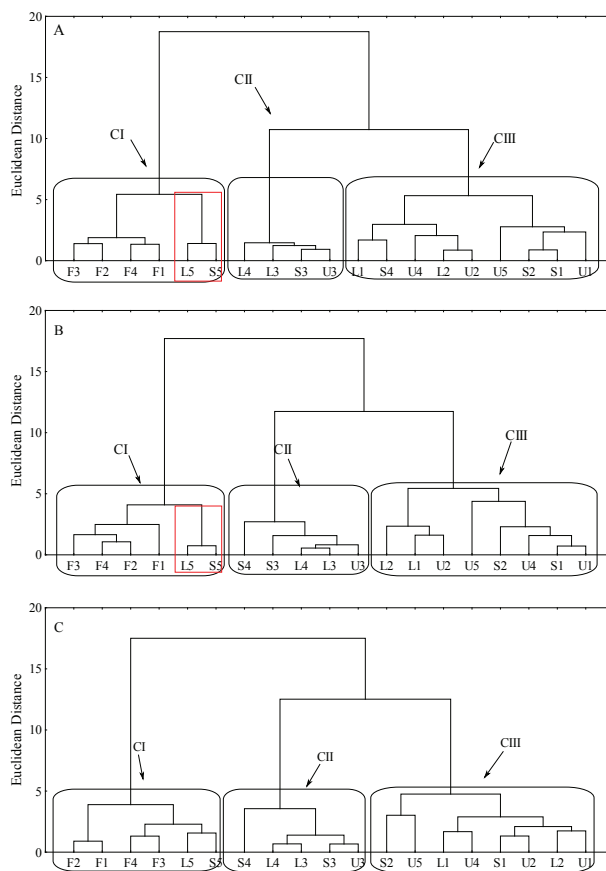

Figure 2. Dendrogram resulting from the Ward's hierarchical clustering of the soil samples, according to the levels of the different contaminants. A = 0.0-0.10 m depth; B = 0.10-0.30 m depth; C = 0.30-0.60 m depth. Segments: upper (U1, U2, U3, U4 and U5); slope (S1, S2, S3, S4 and S5); forest (F1, F2, F3 and F4); lower (L1, L2, L3, L4 and L5).

Table 3. Correlation between principal components, metal content and organic matter in the soil.

Element	0.0-0.10 m depth		0.10-0.30 m depth		0.30-0.60 m depth	
	PC1	PC2	PC1	PC2	PC1	PC2
Cd	-0.276874	-0.913311*	0.106639	-0.946914*	-0.025578	0.954660*
Mn	-0.801896*	0.312220	-0.838754*	-0.013336	-0.775034*	-0.232562
Cu	-0.879429*	-0.368087	-0.817376*	-0.297410	-0.705077*	0.210315
Pb	0.237896	-0.856666*	0.327121	-0.853841*	0.101933	0.846214*
Zn	-0.910359*	-0.162453	-0.665659*	-0.552064	-0.773248*	0.459801
OM	0.661208*	-0.320761	0.823073*	-0.116226	0.806761*	0.376390
P	-0.859509*	-0.074436	-0.845876*	0.205753	-0.413676	0.317507
Ni	0.905545*	-0.134937	0.878241*	0.032135	0.931237*	0.096039

PC1 = principal component 1; PC2 = principal component 2.

most contribute to the total variance of data were the same for all three depths: Mn, Cu, Zn, organic matter and Ni for the principal component 1 (PC1), and Cd and Pb for the principal component 2 (PC2).

The first principal component distinguishes between crop and forest soil samples, and is highly influenced by organic matter and Ni, which has great affinity for binding with organic matter. On the other hand, PC2 suggests an anthropogenic influence for the Cd content, whose accumulation may occur via phosphate fertilization. Cadmium concentrations above the natural levels expected for the areas (Figure 1) and the quality reference values for soils in the Pernambuco State (Pernambuco 2014) corroborate this observation.

With respect to the percentage variance explained by the first principal components, PC1 and PC2 account for 79.11 % at depths of 0.0-0.10 m (54.68 % in PC1 and 24.43 % in PC2), 77.17% at 0.10-0.30 m (51.22 % in PC1 and 25.95 % in PC2) and 69.81 % at 0.30-0.60 m (42.45 % in PC1 and 27.36 % in PC2), respectively (Figure 3).

These results demonstrate the potential of the principal component analysis for this kind of study, reducing the initial seven variables analyzed to only two, which represent well the variance in the original data. There is a clear relationship between Ni and organic matter content in forest areas (L5 and S5). This is due to the high affinity of Ni for organic compounds, such as fulvic and humic acids (Smith 2009, Violante et al. 2010).

By contrast, the segments L1, L2, U1, U2, U4, U5, S1 and S2 were correlated with Cd, Cu, Pb, Zn and P, indicating that these elements may have a common origin via inputs applied to the areas and/ or mixed origins (natural and anthropogenic). This reflects the addition of primarily phosphate fertilizers, since heavy metals are accessory metals in phosphate rocks and are not eliminated in the manufacturing process (Camargo et al. 2000, Costa 2009).

However, given the low P content observed in the forest soil and the low mobility of the element in the soil, it could not be identified at the depth of 0.30-0.60 m for PC1 and PC2. This demonstrates that P does not reflect a natural environment and that the high levels measured (> 40 mg dm^{-3}) (Table 2), considered excessive by Faria et al. (2007) for sandy and clay soils, are of anthropogenic origin. This fact is corroborated by the findings by Costa (2009) and Silva et al. (2010).
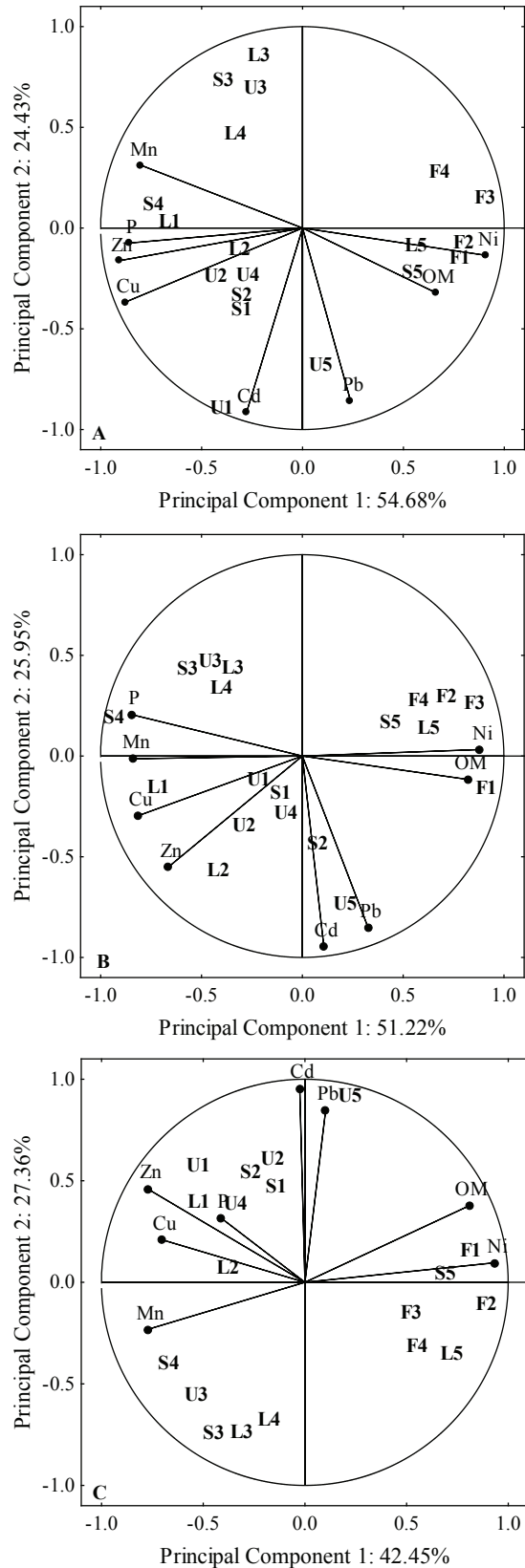

Figure 3. Principal component analysis of elements means in the soil. A = 0.0-0.10 m depth; B = 0.10-0.30 m depth; C = 0.30-0.60 m depth.

CONCLUSIONS

1. Concentrations of Cd, Cu, Mn, P and Zn in cultivated soils are higher than those observed in areas with natural vegetation. This increase is influenced by the soil depth and its position in the transect;

2. The multivariate analysis techniques used are efficient at separating the environments and differentiating the origin of metals. The forest areas are clearly separated from croplands, demonstrating the effect of agricultural practices on the soil metal content and organic matter;

3. Principal component analysis indicated a primarily anthropogenic origin only for Cd, in the most superficial soil layer. The remaining heavy metals showed low contamination risk and are originated primarily from the soil parent material.

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