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Determination of metals in Brazilian soils by inductively coupled plasma mass spectrometry

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Abstract The concentration of metals in Brazilian soil under no-tillage (NT) and an area under native vegetation (NV) was determined by inductively coupled plasma mass spectrometry. The applied method was based on microwave-assisted acid digestion using HNO_3, HCl, H_2O_2, and HF. The accuracy of the method was evaluated by analyzing two certified reference materials (BCR-142 and RS-3). The relative standard deviation for all target elements was below 8 % indicating an adequate precision and the limit of detection ranged from 0.03 $\mu g\ g^{-1}$ (Cd) to 24.0 $\mu g\ g^{-1}$ (Fe). The concentrations of Al, As, Ba, Cd, Cu, Fe, Mg, Mn, Ni, Pb, Sr, and Zn in the different layers (0–10, 10–20, 20–40, and 40–60 cm) were determined in two types of soils, located in Paraná State in Brazil. The soil layers analysis revealed a different behavior of metals concentrations in soil samples under NT and NV. The obtained results showed a clear impact of anthropogenic action with respect to specific metals due to many years of uncontrolled application rates of limestone and phosphate fertilizers.

Keywords Brazilian soils · Soil · Metal · ICP-MS

Introduction

The introduction of potentially toxic elements (PTEs) in the environment is resulting either from natural (mostly geological) inputs or from anthropogenic activities (Frentiu et al. 2013; Álvarez and Garrillo 2012; Esmaeili et al. 2014). The presence of toxic elements in soil is often the result of emissions caused by fuel combustion, industrial activities, and the utilization of agrochemicals such as fertilizers and pesticides (Soodan et al. 2014). However, in order to provide nutrients in adequate amounts and to ensure successful harvests, the use of agrochemicals is essential in some cases; consequently, the long-term application of metal-containing agrochemicals can be potentially damaging (Kelepertzis 2014). Since the elements can be present in soil in different chemical forms reflecting their availability to plants, some toxic elements can be uptaken by plants and enter the food chain (Chand and Prasad 2013). The determination of metals concentrations in soil samples is not a simple task; the high inorganic content of these samples, mainly silicates, makes a time-consuming and sample preparation procedure to solubilize them frequently necessary (Picoloto et al. 2013).

The main soil types used for agricultural production in the region of Campos Gerais are Oxisol, Ultisol, and

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Inceptisol (Distrudept). These soils are typically characterized by high acidity and low fertility (Empresa Brasileira de Pesquisa Agropecuária EMBRAPA 1999). There is little information about the total concentration of the metals in these soils. From this perspective monitoring these elements is necessary, as in some cases these elements can be responsible for the decrease of some plant species, e.g., even barium in tolerable amounts in bean plants may reduce the absorption of potassium in their path leaves (Llugany et al. 2000). Furthermore, the inorganic arsenic is toxic for most of the plants leading to inhibition of phosphate absorption. This can be explained by the chemical similarity between arsenate and phosphate ions (Nascimento et al. 2009). Thus, it is suggested that a high concentration of arsenic in soil can reduce the yield of the plant. In addition, lead can cause many symptoms of toxicity in plants, such as reduced growth, chlorosis, and darkening of the root system. The inhibition of the root growth can be explained by the induced effect of Pb in the root cell division (Sandstorm 2001).

Several methods have been proposed for elemental determination in soil and sediments samples using different analytical techniques, among others atomic fluorescence (AFS), X-ray fluorescence spectrometry (XRF), neutron activation analysis (NAA), atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP OES), or inductively coupled plasma mass spectrometry (ICP-MS) (Soodan et al. 2014; Roje 2011; Melaku et al. 2005). However, ICP-MS is one of the most widely used, apart from its multi-elemental capability this technique offers a high sensitivity, wide dynamic range, isotope ratio information, and the possibility of sample introduction using alternative devices such as electrothermal vaporization (ETV) and laser ablation (LA) (Krishna et al. 2012).

Considering the routine analysis of soil and sediment samples by AAS, ICP OES, and ICP-MS, usually a strongly acid extraction or complete digestion of the sample prior to analysis is required (Picoloto et al 2013; Souza et al. 2014). The procedure for soil and sediment digestion is mainly carried out by alkaline fusion (Uchida et al. 2005), acid digestion using mineral acid and heating with a hot plate (Kelepertzis 2014), or applying a microwave-assisted digestion (Marin et al. 2008; Roje 2011; Melaku et al. 2005). The US Environmental Protection Agency (EPA) has published the methods EPA 3050, 3051, 3051a, and 3052 for acid digestion of soil, sediments, and sludge samples for analysis by AAS, ICP OES, and ICP-MS techniques (Silva et al. 2014). Most of the US EPA methods are not able to promote total sample decomposition, only the microwave-assisted US EPA 3052 in presence of hydrofluoric acid (HF) allows a total sample digestion. Moreover, a high amount of chemicals is needed, according to this method a mixture of 4 mL of hydrochloric acid (HCl), 9 mL of nitric acid (HNO_3) and 3 mL of HF are required for the total sample digestion (Picoloto et al. 2013). Most of the methods are applied for certificate reference samples; consequently, there is a lack of information about concentration of metals in Brazilian soil samples, especially about the soils of Paraná State in Brazil. Thus, this paper proposes the determination of Al, As, Ba, Cd, Cu, Fe, Mg, Mn, Ni, Pb, Sr and Zn concentrations in different layers (0–10, 10–20, 20–40, and 40–60 cm) from the two soil samples under NT and NV area of Paraná State in Brazil.

Experimental

Instrumentation

All the measurements were performed with a Perkin-Elmer SCIEX Elan 6000, inductively coupled plasma mass spectrometer (Perkin-Elmer Sciex, Thornhill, Canada) and Argon (99.996 %, White Martins, São Paulo, Brazil) was used as carrier gas. The optimized instrumental parameters are summarized in Table 1. The monitored isotopes ^{27}Al, ^{75}As, ^{138}Ba, ^{111}Cd, ^{63}Cu, ^{57}Fe, ^{24}Mg, ^{55}Mn, ^{60}Ni, ^{208}Pb, ^{88}Sr, ^{66}Zn were selected in function of their relative abundance and potential interferences. The humidity determinations in soil samples were evaluated by means of a Thermobalance (Top Ray, Bel Engineering) and the sample digestions were carried out in a microwave oven Milestone MLS 1200 Mega model (Sorisole, Italy).

Materials and reagents

All reagents were of at least analytical grade. The water (18 MΩ cm resistivity) was purified in a Milli-Q system (Millipore, Bedford, USA). Nitric and hydrochloric acid (Merck, Darmstadt, Germany) were sub-boiling distilled in a quartz still (Kürner Analysentechnik, Rosenheim, Germany). Hydrofluoric acid 40 %*v*/*v* (Merck, Darmstadt, Germany) was sub-boiling distilled

Table 1 Optimized instrumental parameters for determination of metals in soil

RF power	1100 W
Sampling cone and skimmer	Pt
Sweeps/readings	50
Readings/replicate	1
Replicates	3
Dwell time	25 ms
Plasma gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	1.2 L min^{-1}
Nebulizer gas flow rate	0.92 L min^{-1}
Nebulizer	Cross flow

in a Teflon still (Kürner Analysentechnik, Rosenheim, Germany). Multielement Calibration Standard III and Rh solution (Perkin-Elmer, Shelton, USA) containing 1000 mg L^{-1} were used. Supra-pure hydrogen peroxide 40 %*v*/*v* (VETEC, Duque de Caxias, Brazil) and Boric acid (VETEC, Duque de Caxias, Brazil), as saturated solution 5 %*w*/*v* were used for the fluorine elimination in the digested samples. The soil certified reference material, light sandy soil BCR 142 (Community Bureau of Reference) and a Robin test river sediment sample (RS-3) (Heininger et al. 1998) were analyzed for accuracy evaluation purpose.

Sampling and pretreatment of samples

Soil samples were collected from two soil types, a Rhodic Hapludox (Oxisol) and a Typic Distrudept (Inceptisol) after the 2012/13 crop. From both soils, 4.0 kg were collected, using Dutch auger and paddle court, from the layers 0–10, 10–20, 20–40, and 40–60 cm, situated on a farming area under NT and an NV area. Location data, type of NV, and crop rotation history of the 5 years prior to the collection of samples of each soil are shown in Table 2. For the area under NT, input of nitrogen (N), phosphorus (P), and potassium (K) fertilizers during 5 years, was 548.0 kg ha^{-1} N, 314.0 kg ha^{-1} P, and 355.0 kg ha^{-1} K in Oxisol, and 279.5 kg ha^{-1} N, 371.3 kg ha^{-1} P, and 337.5 kg ha^{-1} K in Inceptisol, respectively. In Table 3, the chemical and granulometric attributes of the two studied soils can be observed.

The soil samples were dried at 40 °C in an oven with forced air circulation, broken apart, ground and sieved through a 2.0-mm-mesh sieve. For the sample digestion procedure, the samples were sieved through a 65 μm mesh sieve and then approximately 0.1 g of soil samples was submitted to a microwave digestion system (MLS-1200, Milestone, USA) using Teflon vessels. Table 4 presents the microwave operational conditions and the used reagents volume. Subsequently, the digested samples were transferred to polyethylene tubes and filled up to 50 mL. The same procedure was adopted for the reference soil samples.

Analytical procedure for analysis by ICP-MS

Trace elements in the digested soil samples were determined by ICP-MS. An adequate aliquot of the digested samples was properly transferred to a 15 mL polypropylene tube and rhodium (Rh) (final concentration of 10 μg L^{-1}) was added as an internal standard and the volume filled up to 10 mL with ultra-pure water. Rhodium was selected as internal standard to correct non-spectral interference and potential sensitivity drift. The calibration curves were based on standard solutions obtained via appropriate dilution of aqueous standard solutions with ultra-pure water. The concentrations of the standard solutions ranged from 1 to 500 μg L^{-1}. The accuracy evaluation was performed by two reference materials, a light sandy soil (BCR 142) and river sediment from a round Robin test (RS-3) (Heininger et al. 1998), submitted to the digestion process described in Table 4 and analyzed in parallel with the soil samples.

Statistical analyses

Data are represented in mean values±standard deviation ($n=3$). Samples were analyzed in triplicate and one paired t test was applied to assess whether the metal concentrations varied significantly between NT and soil from NV. A significant difference was detected at $P<0.05$.

Results

Optimizations

The determination of total element contents in soil samples might be important for a soil characterization. Thus, for the digestion of the complete sample, procedures based on addition of mineral acids mixtures are applied. Moreover, the soil samples have a complex matrix with

Table 2 Location data, type of NV and crop rotation history of the previous five year collection of samples of each soil studied crops

Soil	Localization	Source material	Historic	
			NT[a]	NV[b]
Rhodic Hapludox (Oxisol)	Ponta Grossa—PR S 25° 0′ 28.26″ W 50° 15′ 09.31″	Ponta Grossa Shale[c]	Oat/maize wheat/soybean wheat/soybean oat/maize wheat/soybean	Araucaria Forest Montana
Typic Distrudept (Inceptisol)	Palmeira—PR S 25° 24′ 37.8″ W 49° 58′ 2.8″	Itararé Sandstone[c]	Oat/soybean oat/soybean oat/soybean oat/soybean wheat/soybean	Araucaria Forest Montana

[a] *NT* no-tillage (crop rotation from 2008/09 to 2012/13)

[b] *NV* natural vegetation

[c] Search: Mineropar (2001)

variable composition (Janotková et al. 2013; Wang et al. 2014). Besides the soil matrix, the digested soil sample solutions have a high amount of acid requiring an appropriate dilution before ICP-MS analysis. Consequently, due to the sample matrix complexity, the results of ICP-MS analysis are highly dependent on the instrumental operating conditions. The ICP-MS performance was evaluated by means of daily performance, in order to guarantee the maximum intensities for the analytes ions, low oxide levels, and double-ionized ions. Additionally, for the determination of metals in soil samples, the instrumental parameters of radiofrequency power (RF) and the gas flow rate were optimized. The optimizations were performed using an aqueous standard solution and a soil sample digested for maximum isotopes signal intensities. The RF power was evaluated from 900 to 1400 W with increments of 100 W and the nebulizer gas flow rate was evaluated from 0.8 to 1.3 L min^{-1}, at each 0.1 L min^{-1}. The compromise conditions (1100 W and 0.95 L $\text{min}^{-1}$for RF power and nebulizer gas flow rate, respectively) were selected for the soil sample analyses.

Figures of merit

The figures of merit for soil analyses by ICP-MS using external calibration with aqueous standard solutions and Rh as internal standard were satisfactory for the soil analysis. The linear correlation coefficients for ICP-MS were good for all analytes (R>0.999). The precision was estimated by the relative standard deviations (RSD) which were lower than 8 % (n=3) indicating a reasonable precision for a multi-elemental analysis. For determining the limit of detection (LOD), the dried sample in view of an aliquot of 0.1 g of soil sample digested in a 50-mL final volume solution and a dilution of 10 times prior to ICP-MS analysis was considered. The LOD was defined as three times the standard deviation of ten measurements of the blank divided by the slope of the calibration curve, and the LOD values are shown in

Table 3 Chemical and physical analysis of the soil at the collection after 2012/13

Soil	Chemical analysis			Physical analysis		
	pH[a]	CEC[b] $\text{mmol}_c\ \text{dm}^{-3}$	C org[c] g dm^{-3}	Clay g kg^{-1}	Silt	Sand
Rhodic Hapludox (Oxisol)	3.8	166.1	33.0	736.0	174.2	89.8
Typic Distrudept (Inceptisol)	4.3	145.6	21.0	200.0	255.2	544.8

[a] pH of a solution of calcium chloride 0.01 mol L^{-1}

[b] CEC: cation exchange capacity (sum of the contents of calcium, magnesium, and potassium exchangeable over the value of potential acidity (H + Al))

[c] C org = the soil organic carbon content

Table 4 Reagents and operating condition for microwave soil sample digestion

Digestion reagents			Microwave program		
Reagents	Volume (mL)	Step	Temperature 1 (°C)	Temperature 2 (°C)	Hold time (min)
HNO_3	4	1	20	85	2:30
HCl	1	2	85	150	4:00
H_2O_2	1	3	150	210	5:00
HF	0.5	4	210	210	20:00
		5	Cooling down		
H_3BO_3[a]	4	–			

[a] H_3BO_3 was added and the microwave program was performed again for the fluoride elimination

Table 5. The LOD obtained was below 7.3 μg g^{-1} for all elements; these values are comparable to or even better than those found in literature, using a similar sample pretreatment and ICP-MS analysis. The limit of quantification (LOQ) was defined as 3.3 times the LOD. The obtained LOQ for the applied method values was from 0.03 μg g^{-1} for Cd to 24.0 μg g^{-1} for Fe, being adequate for the analyzed soil samples.

Accuracy

The accuracies of the procedures were estimated by the analysis of two reference materials: the light soil BCR 142 and the river sediment RS-3. As shown in Table 6, the results obtained using the two reference samples are in agreement with the certified values, according to the *t* test for a confidence level of 99 %. The obtained concentrations for Pb and Zn in RS-3 were slightly lower than the results shown in the certificate; however, the concentration of these elements in the sample BCR-142 was in perfect agreement with the certificate concentration. Moreover, a good agreement was achieved with the values obtained by the proposed method for Al, Ba, and Sr, in BCR-142, with the informed concentration (estimated concentration values), indicating the accuracy of the proposed method for these elements. Thus, the method can be considered precise and accurate for determination of these elements in soil samples by ICP-MS.

Table 5 Limit of detection for the determination of elements by ICP-MS in soil sample, using external calibration

Isotopes	This work	(Roje 2011)	(Melaku et al. 2005)
^{27}Al	2.40	16.3	–
^{75}As	0.70	0.17	–
^{138}Ba	0.40	1.17	–
^{111}Cd	0.01	0.04	0.01
^{63}Cu	0.06	0.89	0.03
^{57}Fe	7.30	1.89	–
^{24}Mg	1.70	–	–
^{55}Mn	0.04	1.0	0.02
^{60}Ni	0.20	0.28	0.04
^{208}Pb	0.01	0.40	0.01
^{88}Sr	0.05	3.39	–
^{66}Zn	0.35	2.31	2.3

Measurement results

The method was applied for determination of metals in two different types of soil samples (Oxisol and Inceptisol) from Paraná state in Brazil collected in different layers. In Fig. 1, the results for Oxisol soils are presented and as can be observed the concentrations for Cd, Cu, Mn, Pb, Sr, Zn were significantly higher in soils under NT than those in soils under NV. Ni showed similar behavior; but in the concentration obtained from the layer 10–20 cm, no significant difference was observed. On average, the results achieved for As were higher in NT soils, showing significance in the 10–20 cm and 20–40 cm layers.

The highly weathered Brazilian soils (e.g., Oxisols) have low P concentrations and high acidity. Therefore for these soils large amounts of limestone and phosphate fertilizers have been used to maximize farm income. However, the mineral raw material for phosphate fertilizer may contain As, Cd, Cu, Mn, Ni, Pb, and Zn as contaminants (Malavolta 2006). Strontium is one of the contaminants of agricultural limestone (Liu et al. 2013; Brinza et al. 2013). Thus, the levels of As, Cd, Cu,

Table 6 Obtained concentrations (average±ts; n=3; 95 % confidence level) and certified or informed values from BCR 142 and RS-3

	RS-3 (μg g^{-1})		BCR-142 (μg g^{-1})	
	Certified value	Determined	Certified value	Determined
Al (%)	4.07±0.10	4.55±0.93	5.01[a]	3.98±0.32
As	16.4±0.5	20.08±1.44	16[a]	17.05±1.45
Ba	–	830.30±37.20	450[a]	363.54±27.51
Cd	3.93±0.06	3.72±0.49	0.25±0.09	0.31±0.01
Cu	154.4±1.2	149.81±11.00	27.5±0.6	27.50±3.52
Fe (%)	3.16±0.05	3.26±0.52	1.96[a]	1.89±0.19
Mg (%)	0.96±0.02	0.87±0.09	6570[a]	5563±794
Mn	900±12	806.51±106	–	591.60±26.07
Ni	82.4±1.0	84.68±4.40	29.2±2.5	29.70±3.40
Pb	129.0±1.7	100.28±15.74	37.8±1.9	38.72±3.52
Sr	–	230.76±10.45	164[a]	145.43±9.00
Zn	1129±7	1038±44	92.4±4.4	85.92±6.10

[a] Informed values

Mn, Ni, Pb, Zn, and Sr elements in soils under NT are probably due to the use of limestone and phosphate fertilizers. Magnesium showed significantly higher concentration in NV soils only in the first layer (0–10 cm). In the upper soil layers, the biological activity and the biogeochemical cycling of elements is usually higher, playing an important role in maintaining NV. This justifies higher concentration of elements in the 0–10 cm layer for Mg, about everything in highly weathered soil (Oxisol) (McLaughlin et al. 2011).

The iron concentration in both Oxisol soils (NV and NT) was very similar, but the layer 20–40 cm showed significantly higher values for NT soils. For Al, the concentrations were found at level of mg g^{-1} for both

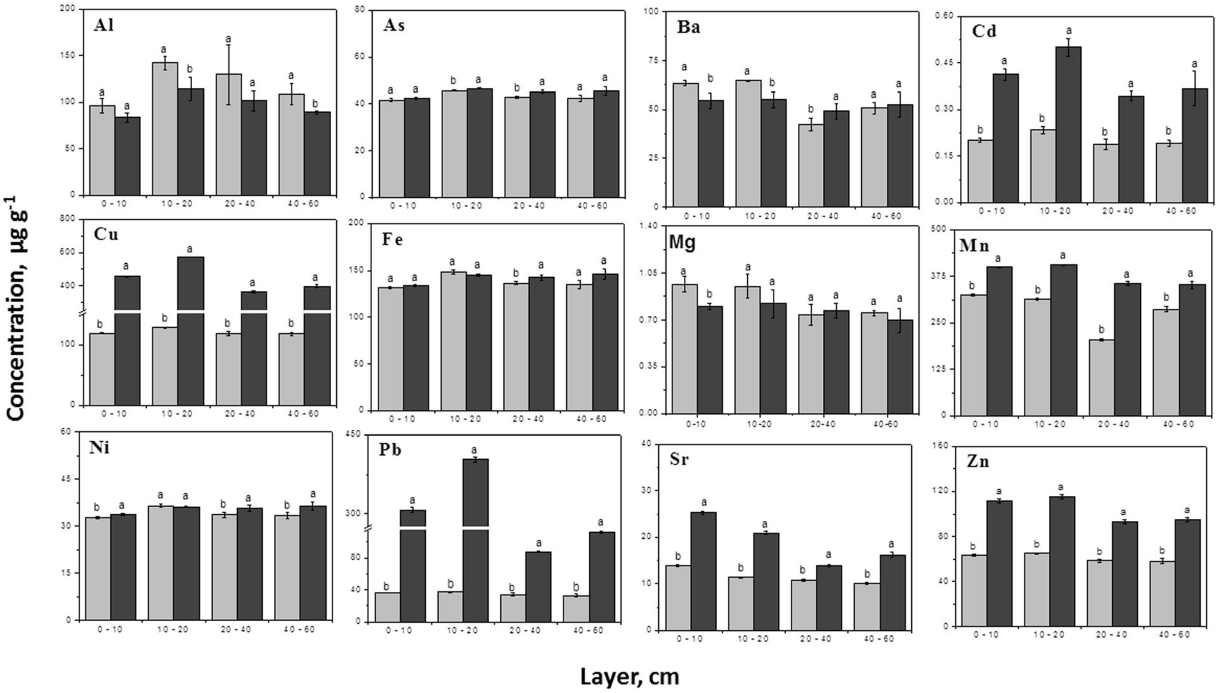

Fig. 1 Results for Oxisol (Rhodic Hapludox) soil samples, average ± standard deviation (μg g^{-1}) in dry weight. Under NV ▨ and (NT ■. *Bars with different letters* show significant difference. *Al, Mg, and Fe concentration in milligrams per gram

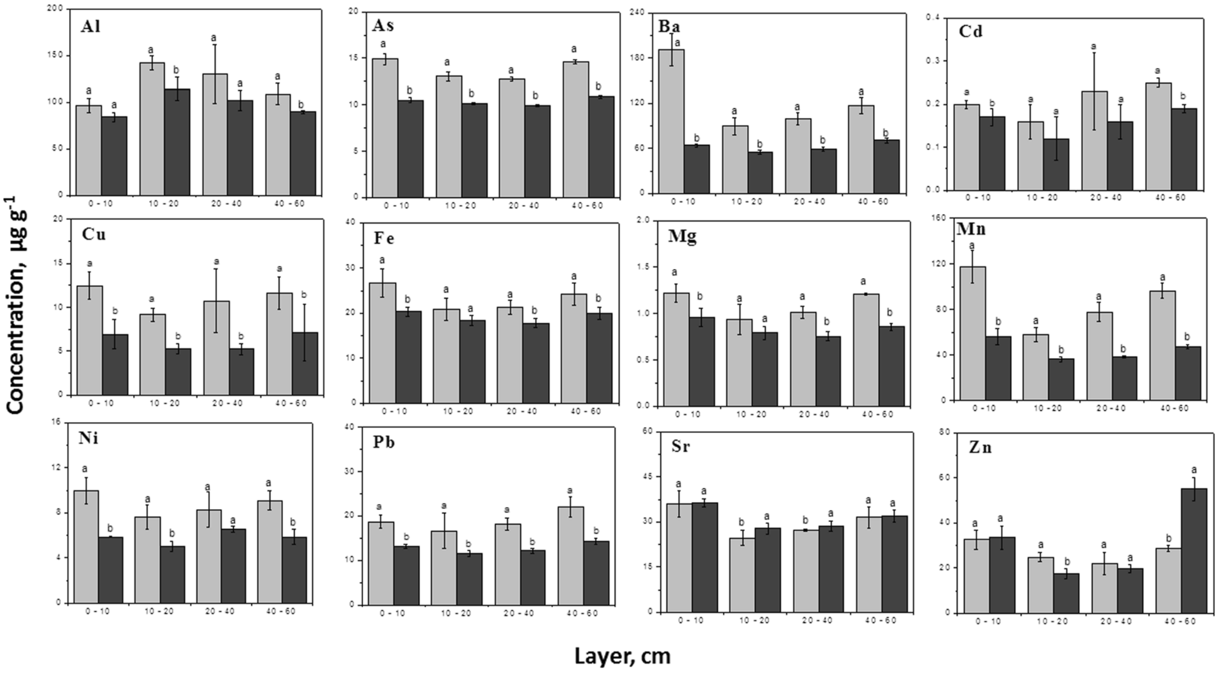

Fig. 2 Results for Inceptisol (Typic Distrudept) soil samples, average ± standard deviation (μg g^{-1}) in dry weight. Under NV ░ and NT ■. *Bars with different letters* show significant difference. *Al, Mg, and Fe concentration in milligrams per gram

analyzed soils. However, the concentrations of Al found in soils under NV showed higher results when compared with soils under NT soil. In agricultural soil under NT a larger elements removal due to harvesting occurs causing a reduction of the stocks of elements in the system, such as Fe and Al which are not reintroduced through fertilizers and corrective components. Furthermore, the iron concentrations in Inceptisol were much lower in comparison with those of Oxisol samples. This behavior was expected since Inceptisol is characterized by high iron concentration due to its source material (Table 2).

The obtained results for Inceptisol samples (Fig. 2) generally show that the element contents of As, Cd, Cu, Mn, Ni, Pb, and Zn, were lower concentrations than those found in Oxisol samples. In intrazonal soils with little weathering (as Inceptisol), the application of phosphate fertilizers and corrective compounds of PTE (Malavolta 2006; Liu et al. 2013; Brinza et al. 2013) have been lower. This justifies the fact that in the Inceptisol the element concentrations were not altered and mostly did not show lower concentrations of PTE in NT samples. Moreover, the highest concentrations for almost all analyzed elements were found in soils under NV, except for Zn showing a significantly higher concentration under NT soil in layer 40–60. This increase in Zn may be due to the addition of fungicides. Crops of wheat and soybeans have shown frequent occurrences of fungal diseases, normally controlled with Zn-based fungicides (Food and Agriculture Organization of the United Nations FAO 1980).

According to Conselho de Política Ambiental (COPAM), the reference values of As, Cd, Cu, Mn, Ni, Pb, Zn, and Sr are 35, 3, 200, 150, 70, 180, 450, and 50 mg kg^{-1}, respectively (Brinza et al. 2013; Conselho de Política Ambiental COPAM 2011; Biondi et al. 2011; Sociedade Brasileira de Ciência do Solo SBCS 2013). The agricultural cultivation of the soil under NT resulted in changes in the concentration of these elements but did not reach the reference values for Inceptisol. However, in Oxisol, the concentrations of As, Cu, Mn, and Pb were higher than the reference values, but not enough to be considered as concentrations characteristic of polluted soil.

Conclusion

The acid digestion used a microwave oven and can be considered efficient, quick, and simple to determine multi-elements in soils, since it shows relatively low standard deviations and good accuracy. Furthermore, with this study, it was possible to delineate the accumulation and identify the sources of heavy metals in agricultural soils from the Paraná state, which is one of Brazil's agricultural powerhouses. The results highlight a clear impact of anthropogenic activity with respects to the occurrence of specific metals (As, Cd, Cu, Mn, Ni, Pb, and Zn) found in Oxisol due to many years of uncontrolled application rates of limestone and phosphate fertilizers. In the Inceptisol, the concentrations of metals were lower probably due to a lower consumption of chemical fertilizers and soil additives. However, the concentration levels found in all samples cannot be considered as contaminations, because their values are lower than the Normativa no 166 of 2011 reference values. The results of this study will provide land managers with valuable data of potentially toxic and non-toxic elements for the current qualitative status of the studied soils that should be taken into account for monitoring heavy metal levels and reducing application rates of agrochemicals.

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