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Article

Distribution and Availability of Copper, Iron, Manganese and Zinc in the Archaeological Black Earth Profile from the Amazon Region

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Os solos de terra preta arqueológica são ricos em matéria orgânica, contêm fragmentos cerâmicos e artefatos líticos e apresentam nutrientes em concentrações mais elevadas do que outros tipos de solos. Com o intuito de contribuir com informações sobre concentrações de micronutrientes disponíveis em solos de terra preta, foram avaliadas através de extrações químicas sequenciais, a distribuição e disponibilidade de Cu, Fe, Mn e Zn em um perfil de terra preta arqueológica no município de Juruti, estado do Pará. As maiores concentrações de Cu, Fe, Mn e Zn no perfil são encontradas na fração residual. Este estudo mostrou que ferro, manganês e zinco são preferencialmente disponíveis a partir das frações, associados aos óxidos de Fe-Mn, variando de 1265,39 a 1818,12 mg kg^{-1}, 0,83 a 48,51 mg kg^{-1} e 1,92 a 12,05 mg kg^{-1}, respectivamente, e o cobre a partir da matéria orgânica, variando de 0,13 a 0,45 mg kg^{-1}.

The archaeological black earth soils are rich in organic matter, contain ceramic fragments and lithics artifacts and feature nutrients in higher concentrations than other types of soils. To contribute information about micronutrient concentrations available in black earth soils, the distribution and availability of Cu, Fe, Mn and Zn in the archaeological black earth profile from the municipal district of Juruti, Pará State, was evaluated through sequential chemical extractions. The largest concentrations of Cu, Fe, Mn and Zn in the profile are found in the residual fraction. This study showed that the iron, manganese and zinc are preferentially available from the fractions associated with Fe-Mn oxides ranging from 1265.39 to 1818.12 mg kg^{-1}, 0.83 to 48.51 mg kg^{-1} and 1.92 to 12.05 mg kg^{-1} respectively, and the copper from organic matter, ranging from 0.13 to 0.45 mg kg^{-1}.

Keywords: archaeological black earth, distribution, metals, availability, FAAS

Introduction

The *terra preta* anthrosols of Amazonia are mainly oxisols, ultisols and inceptisols with an anthropic A horizons[1] with dark colouration, popularly called idian black earth (IBE) or archaeological black earth (ABE),[2] occur mainly in the Brazilian Amazon, Colombia, and, less frequently, Venezuela, Peru, and Guiana.[3] The areas in which ABE occurs is characterized by well-drained soil, running water and located in a particular geographical setting from which the surrounding areas can be clearly observed.[4] Several hypotheses have been suggested on the process of ABE formation; however, the most widely accepted states that ABE would have been formed unintentionally by pre-Columbian man.[5] Human activity in the pre-Columbian past has resulted in the accumulation of plant and animal residues, as well as large quantities of ceramic and lithic artifacts, ash, charcoal, and various chemical elements, such as P, Mg, Zn, Cu, Ca, Sr and Ba, representing the geochemical signature of human occupation. These accumulations probably contributed decisively to the formation of fertile soils,[6] with high concentrations of available phosphorus and calcium and low concentrations of Al (III) cause the plants to develop better in black earth[7] compared with the adjacent non anthropogenic soils.

Several chemical elements in soils are physiologically essential for growth and vegetal reproduction.[8] Elements such as copper, iron, manganese, and zinc are essential to biological systems, but can produce toxic effects when

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absorbed in high quantities;[9] therefore, knowledge on the availability of these elements in soil is of fundamental importance.

The total content of metals in soil is generally not a suitable index for estimating their availability in soils, because only part of them is mobile in the soil profile and is available for absorption by the roots of plants.[10] These metals can accumulate in the soil in different forms such as water-soluble, exchangeable, bound to oxides, bound to carbonates, and bound to organic and residual matter in the structure of minerals.[11] Water-soluble and exchangeable fractions are considered readily mobile and available; fractions associated to oxides, carbonates, and organic matter may be potentially available,[12] depending on the combination of chemical and physical properties of the soil,[10] while the residual fraction is not available to plants and microorganisms.[12] One of the tools used to evaluate the different chemical forms of metals in soil is the sequential extraction methods.[11] These methods are commonly used for the fractionation of metals in soils, sediments, and other environmental matrices and to evaluate the potential mobility and availability of these metals.[13] The principle of the sequential extraction method consists of sequentially applying appropriate chemical reagents, where each step of the sequence is chemically more aggressive than the previous one.[14] Each method has a set of reagents which specifically attacks the geochemical form by which it is chemically bound to the soil structure.[11] The information obtained allows the phyto-bioavailability, phytotoxicity, dynamics of trace elements, and transformations between the different chemical forms in polluted or tillable soils to be assessed.[15]

The aim of this study was to evaluate the distribution and availability of copper, iron, manganese, and zinc among different fractions in the soil profile of ABE from Juruti-PA.

Experimental

Study area

The study was conducted with archaeological black earth (ABE) profile samples obtained in the *terra preta* archaeological site 2, in the rainy season, in an area in the municipality of Juruti (PA) on the right bank of the Amazon River. Located in the western State of Pará, Brazil, the municipality has an estimated population of 38,000 inhabitants in an area of 8342 km², 848 km away from the capital Belém. Prospecting site *terra preta* 2 was based on the application of systematic sampling distributed in vertical lines, towards the east. Along these lines, towards the south, were made polls belonging to lines 480E, 360E, 240E, 120E, according to the Figure 1. For a refined understanding of archeological study, three areas were opened called excavation unit 1, 2 and 5. Furthermore, it was opened a soil profile, object of study of this work, which was described and collected following the soil horizons. The location of the soil profile is at the geographical coordinates UTM 21M 599557E and 9759353N.

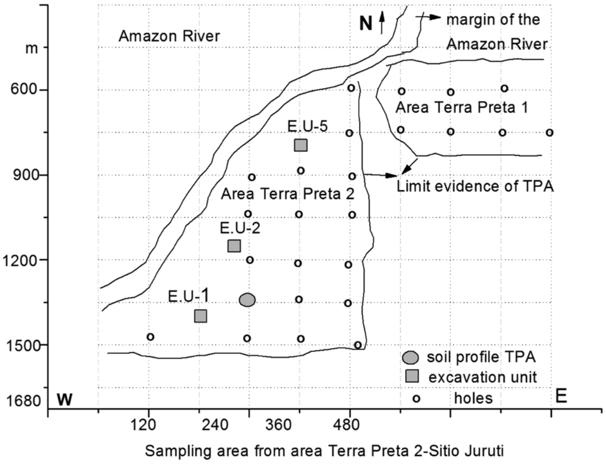

Figure 1. Location of black earth site 2 in the municipality of Juruti.

Soil samples

Morphological description of soil horizons were classified according to standards recommended by the Brazilian Society of Soil Sciences[16] and colors samples were determined according to Munsell.[17] Soil samples were air dried, lumps were removed, and the samples were passed through a 2 mm sieve. The pH values in water and organic matter were determined according to the methods of Embrapa.[18] The pH of samples in water was determined by the direct potentiometric method using a soil:water ratio of 1:2.5 after 1 h of rest and shaking before reading. The organic matter content was determined by the oxidation-reduction method using potassium dichromate as the oxidant of organic matter.

Reagents and materials

All solutions were prepared using deionized water (resistivity of 18.2 MΩ cm) purified by an ELGA system (Elgastat, Bucks, England). For extraction procedures, the following analytical grade reagents were used: magnesium chloride ($MgCl_2$, Nuclear, São Paulo, Brazil), sodium acetate (NaOAc, Nuclear), hidroxylamine chloride ($NH_2OH{\cdot}HCl$, Nuclear), acetic acid (HOAc, Impex, São Paulo, Brazil), hydrogen peroxide (H_2O_2, Impex) ammonium acetate (NH_4OAc, Vetec, Rio de Janeiro, Brazil), nitric acid (HNO_3 65% v/v, Impex), hydrochloric acid (HCl 37% v/v, Impex) and hydrofluoric acid (HF 40% v/v, Quimex, São Paulo, Brazil).

Appropriate buffer solutions (pH 4.0 and pH 7.0) were used for calibrating the pHmeter.

The analytical curves were prepared from standard solutions of 1000 mg L^{-1} for all elements (J. T. Baker). All glassware and bottles used in the procedures were immersed in 10% (v/v) HNO_3 solution for 24 h and thoroughly rinsed with deionized water.

The sequential extractions were performed using horizontal mechanical shaker Model 3520 (LAB-Line, USA) and centrifuges Model 80-2B (Centribio, Brazil)

Analytical procedure

Sequential extraction

The sequential extraction procedure of Ma and Rao,[19] which is a modified version of the method described by Tessier *et al*.,[11] was used to separate the metals into six fractions which were denoted as F1, F2, F3, F4, F5, and F6.

Approximately 1 g of each sample from the ABE profile was weighed in triplicate and transferred to centrifuge tubes of 15 mL and then the following sequential extraction was carried out. (*i*) Water-soluble fraction (F1): the soil was extracted with 10 mL of deionized water for 2 h in a horizontal shaker at room temperature. (*ii*) Exchangeable fraction (F2): the residue obtained in F1 was extracted with 10 mL of $MgCl_2$ solution 1.0 mol L^{-1} (pH 7.0) for 1 h in a horizontal shaker at room temperature. (*iii*) Fraction bound to carbonates (F3): the residue obtained in F2 was extracted with 10 mL of sodium acetate solution (NaOAc) 1.0 mol L^{-1} (pH 5) for 5 h in a horizontal shaker at room temperature. (*iv*) Fraction bound to Fe-Mn oxides (F4): the residue obtained in F3 was extracted with 10 mL of hydroxylamine chloride solution ($NH_2OH{\cdot}HCl$) 0.04 mol L^{-1} in acetic acid (HOAc) 25% (v/v) for 5 h at 96 °C under slow agitation. (*v*) Fraction bound to organic compounds (F5): the residue obtained in F4 was extracted with 10 mL H_2O_2 30% (m /m) at pH 2.0 (adjusted with HNO_3) for 5.5 h in a water bath at 85 °C under slow agitation. After this time, the samples were cooled, 2.5 mL of ammonium acetate (NH_4OAc) 3.2 mol L^{-1} in HNO_3 20% (v/v) were added, and samples were then stirred for 30 min. (*vi*) Residual fraction (F6): the residue obtained in F5 was placed to dry in oven at 60 °C for 24 h and removed from the centrifuge tubes. The digestion of the residue was performed by adding 16 mL of Lefort water ($3HNO_3$:1HCl), and after 12 h of rest the samples were heated for 8 h at a temperature of 160 °C. The digested part and the residue (silicate compounds that were not digested) were quantitatively transferred into a centrifuge tube of 50 mL with the addition of 10 mL of deionized water. The separation of the supernatant and residue was carried out by centrifugation at 2000 rpm for 5 min. The residue was dissolved at room temperature by adding 2 mL of concentrated HF, and after dissolution, 1 g of H_3BO_4 was added for the complexation of the remaining fluoride. The resulting mixture was added to the previously collected supernatant (liquid phase of the digested part) and the volume was adjusted to 50 mL with deionized water.

At the end of each extraction process (fractions F1, F2, F3, F4, and F5), the separation of the residue and supernatant was carried out by centrifugation at 3000 rpm for 30 min. The supernatants were removed with a pipette and filtered through Whatman filter paper no. 42. All solid phases were washed with 5 mL of deionized water before the next extraction. Washes were collected and analysed with the supernatant from the previous fraction. All experiments were performed in triplicate.

Instrumentation

All determinations of metals were performed using a flame atomic absorption spectrometer (FAAS) (Model AA 220, Varian, Australia) equipped with Cu, Fe, Mn and Zn hollow cathode lamps and an air-acetylene flame. The instrumental conditions are shown in Table 1.

Table 1. Operational condition for FAAS

Parameters	Cu	Fe	Mn	Zn
Wavelength / nm	324.8	248.3	279.5	213.9
Lamp current / mA	4.0	14.0	15.0	10.0
Spectral resolution / nm	0.5	0.2	0.2	1.0

Addition of 4.0 mg L^{-1} Cu, 9.0 mg L^{-1} Fe, 2.0 mg L^{-1} Mn, and 1.0 mg L^{-1} Zn and recovery tests were performed to all fractions studied.

Results and Discussion

Organic matter content and pH

The ABE profile analysed reaches beyond 150 cm deep and presented an A1 horizon with 12 cm thick, black color, some ceramic fragments and many fine roots. The A2 horizon presented a thickness of 35 cm, dark brown color, some ceramic fragments, coal, and many fine roots. The A3 horizon presented a thickness of 73 cm, very dark grayish brown, some ceramic fragments and coal. While the horizons of transition AB and BA occupy the depth range between 75 and 130 cm and their colors range from yellowish brown to dark brown, respectively. The B horizon extends beyond 150 cm and showed a yellowish brown color. The pH and organic matter content determined in *terra preta* soil samples are presented in Table 2. The *terra preta* soil profile had pH values in the range from 4.97 to 6.07. These soils are classified as from high acidity to weak acidity, and the values increase with depth. In relation to organic matter content, the values obtained for the soils studied were greater than 76.31 g kg^{-1}. These values are higher than those obtained by Lemos *et al.*[20] from areas with ABE in Ilha de Terra site in the Caxiuanã region (PA) and were also higher than values found in the high concentration class, according to Tomé Jr.[21]

Table 2. Chemical soil attributes

Samples	pH ± SD^a	O.M. ± SD^a / (g kg^{-1})
A1	4.97 ± 0.01	80.10 ± 5.35
A2	5.57 ± 0.01	81.95 ± 4.22
A3	5.90 ± 0.01	80.15 ± 1.17
AB	6.08 ± 0.01	76.31 ± 0.14
BA	5.67 ± 0.02	81.55 ± 0.84
B	5.52 ± 0.02	81.80 ± 1.17

^{a}SD = standard deviation (n = 3).

Distribution of metals in the ABE profile

Sequential extraction is useful to indirectly assess the potential mobility and availability of metals in soils. Assuming that availability is related to solubility, it can be inferred that the metal availability decreases in the following order: water-soluble > exchangeable > carbonate > Fe-Mn oxides > organic > residual. This order provides only qualitative information about the metal availability. It can also be inferred that the metal in the non-residual fraction is more available than the metal associated to the residual fraction. The non-residual fraction is the sum of all the fractions less the residual fraction.[19]

Copper

The result of the percentage distribution among the copper forms held in the ABE profile (Figure 2) indicates that this element was recovered (39.70-62.48%) in the residual fraction (F6) and in the fraction bound to organic compounds (F5) (34.90-53.47%). A low Cu percentage (2.16-5.82%) was found in the fraction bound to Fe-Mn oxides (F4). The Cu contents in the fractions of water-soluble (F1), exchangeable (F2), and associated to carbonates (F3) were below of the limit of detection, except for the water-soluble fraction of sample A$_1$ (0.98% of total Cu).

The high Cu content obtained in the residual and organic soil fractions has been reported by other authors.[19,22,23] This association of copper with the organic fraction confirms the ability of this metal to form stable complexes with organic matter through reactions with COOH groups and phenolic OH.[24]

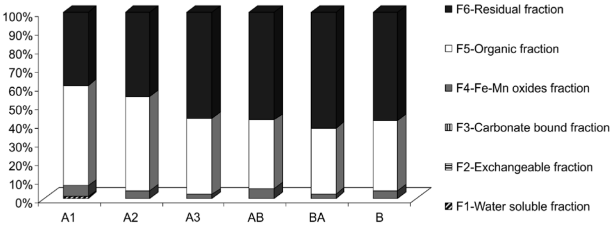

Figure 2. Percentage distribution of copper in soil chemical fractions.

Table 3 shows the Cu contents that were extracted from fractions of the ABE profile. It can be observed that in the fractions associated to Fe-Mn oxides, the organic matter and residual were obtained higher extractions in the A$_2$ horizon. In the water-soluble fraction, only a low Cu content was detected in the A$_1$ horizon.

In the A$_1$ and A$_2$ surface horizons, it was noticeable that there is a greater affinity of Cu for the fraction associated with organic compounds, while in the A$_3$, AB, BA, and B subsurface horizons the affinity is for the residual fraction. As the ABE profile deepens, copper becomes more stable, or unavailable to plants. About the level of toxicity to plants, Cu levels obtained in the sum of fractions F1, F2, F3, F4, and F5 showed adequate levels.[25]

According to Wedepohl,[26] in the upper continental crust, Cu presents a total content of 14.30 mg kg^{-1} soil. Taking this value as reference, it can be observed that the levels found in the sum of fractions are in agreement with this value.

Analysis of coefficient of variation for all fractions studied showed variations between 53.39% for fraction bound of Fe-Mn oxides to 26.58% for residual fraction, evidencing the variability of Cu, along the soil profile.

The amount of Cu found in the non-residual fractions ranged from 37.52% in the BA horizon to 60.30% in the A$_1$ horizon. These data are compatible with results obtained for Cu available from other sites of the ABE.[27,28] Among the non-residual fractions, the fraction bound to organic matter had the greatest levels of Cu extracted throughout the ABE profile. It can be inferred that the availability of this element in the soil depends on the organic matter content.

Table 3. Content of copper (mg kg^{-1} ± SD^{a}) extracted in each fraction of soil samples

	Soil profile					
Fraction	A1	A2	A3	AB	BA	B
Water soluble	0.07 ± 0.02	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*
Exchangeable	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*
Carbonate	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*	< 0.01*
Fe-Mn oxide	0.45 ± 0.06	0.45 ± 0.04	0.16 ± 0.04	0.29 ± 0.04	0.13 ± 0.07	0.16 ± 0.01
Organic	4.10 ± 0.32	5.38 ± 0.94	3.11 ± 0.92	1.88 ± 0.06	1.98 ± 0.11	1.50 ± 0.15
Residual	3.04 ± 0.03	4.85±0.45	4.35 ± 0.12	2.99 ± 0.40	3.51 ± 0.02	2.34 ± 0.26
Sum of all fractions	7.68	10.68	7.63	5.17	5.63	4.01
Non-residual / (%)	60.30	54.53	42.97	42.04	37.52	41.51
Residual / (%)	39.70	45.47	57.03	57.96	62.48	58.49

^{a}SD = standard deviation (n = 3); *LOD (limit of detection) / (mg L^{-1}).

Iron

The result of the percentage distribution between the forms of Fe obtained in the ABE profile (Figure 3) shows that the residual form (F6) is dominant, with percentages ranging from 80.18 to 89.34%. A significant proportion of Fe in the soil profiles (8.99 to 17.29%) was obtained in the fraction associated with Fe-Mn oxides (F4). This relationship was expected, since this element is found in soil, mainly in the forms of oxides and hydroxides.[29]

In the water-soluble fraction (F1), a low percentage of total Fe (0.13 to 2.42%) was obtained in the studied profile. However, in the form bound to organic matter (F4), less than 0.40% of the total Fe was found, while in exchangeable fractions (F2) and those associated with carbonate (F3), the percentages were < 0.28%.

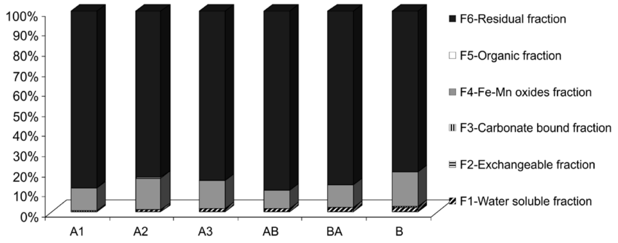

Figure 3. Percentage distribution of iron in soil chemical fractions.

Table 4 shows the Fe contents obtained in fractions from the ABE profile. It was observed that in water-soluble, exchangeable, and residual fractions, the highest total Fe contents were obtained in the AB horizon. In the fraction bound to carbonates, a higher Fe extraction was obtained in the A$_1$ horizon, with its amount decreasing with depth in the fraction.

For fractions associated with Fe-Mn oxides and organic matter, major extractions were obtained in the A$_2$ horizon.

About the levels of toxicity to plants, Fe levels obtained in the sum of fractions F1, F2, F3, F4, and F5 showed adequate levels.[30]

According to the value found in the upper continental crust,[26] iron has a total content of 30.890 mg kg^{-1} soil, and considering this value as reference, it may be noted that the levels found in the sum of fractions in the studied profile are in accordance with this value.

The coefficient of variation for almost all fractions remained on area high dispersion, ranging from 13.70% to 76.0%, evidencing the variability of Fe among fractions, along the soil profile.

The Fe levels present in the non-residual fractions showed variations between 10.66% in the AB horizon and 19.82% in the B horizon. Among the non-residual fractions, the fraction bound to Fe-Mn oxides showed the highest Fe content throughout the profile. Therefore, this fraction is the immediate reserve for the supply of this element in the ABE profile.

Manganese

The result of the percentage distribution between the forms of Mn found in the ABE profile (Figure 4) shows that this element had the most even distribution among the fractions analysed. Considerable quantities of total Mn were found in residual (F6), bound to Fe-Mn oxides (F4) and to organic matter fractions (F5), with percentages ranging from 18.19 to 60.06%, 8.99 to 56.18%, and 0.92 to 55.71%, respectively.

It may be noted that the lowest distribution of total Mn was obtained in fractions which were bound to carbonates (F3) (4.52-12.65%) and water-soluble (F1) (1.44-3.43%). The contents in the exchangeable fraction (F2) were below the detection limit, with the exception of the sample from the A$_1$ surface horizon, which showed 16.06% of total Mn.

Table 4. Content of iron (mg kg^{-1} ± SD[a]) extracted in each fraction of soil samples

	Soil profile					
Fraction	A1	A2	A3	AB	BA	B
Water soluble	15.08 ± 0.64	112.37 ± 1.19	170.79 ± 1.42	292.98 ± 69.32	272.37 ± 47.55	192.31 ± 0.93
Exchangeable	2.38 ± 0.15	< 0.12*	0.42 ± 0.10	2.89 ± 0.11	2.68 ± 0.02	2.10 ± 0.07
Carbonate	31.68 ± 0.70	21.65 ± 0.72	18.19 ± 0.46	10.17 ± 0.21	8.02 ± 0.65	4.86 ± 0.39
Fe-Mn oxide	1265.39 ± 227.55	1818.12 ± 345.53	1497.66 ± 131.49	1749.72 ± 8.19	1599.41 ± 32.23	1376.43 ± 57.17
Organic	34.12 ± 2.47	46.03 ± 13.08	21.25 ± 0.64	19.07 ± 1.03	5.79 ± 0.25	2.68 ± 0.06
Residual	9847.76 ± 671.20	9507.49 ± 968.56	9241.05 ± 662.06	17391.25 ± 2444.06	12123.86 ± 1458.76	6384.52 ± 815.11
Sum of all fractions	11196.42	11505.66	10949.37	19466.08	14012.14	7962.89
Non-residual / (%)	12.05	17.37	15.60	10.66	13.48	19.82
Residual / (%)	87.95	82.63	84.40	89.34	86.52	80.18

[a]SD = standard deviation (n = 3); *LOD (limit of detection) / (mg L^{-1}).

Soil pH is, in most cases, the main factor controlling the availability of micronutrients for plants,[31] and the availability of these metals is relatively low at pH values around 6 to 7.[32] About the levels of toxicity to plants, Mn levels obtained in the sum of fractions F1, F2, F3, F4, and F5 showed adequate levels.[25]

It can be observed that in the fraction bound to organic matter, the percentages of total Mn increased with the profile depth, which may be due to pH increases along the ABE profile. Under these pH conditions (around 6) the amount of Mn adsorbed by the organic matter is generally high, and there are usually low contents of exchangeable forms and high contents of organic forms and oxides,[33,34] which agrees with the results of this study.

In the A_1 and A_2 horizons, the sum of total Mn obtained in F1, F2, and F3 was higher than 16.00%. This suggests that Mn in the surface horizons may be highly available in the ABE profile.

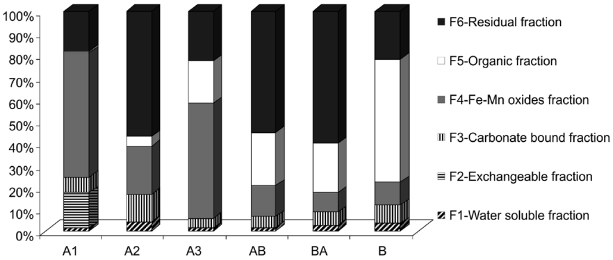

Figure 4. Percentage distribution of manganese in soil chemical fractions.

Table 5 presents the Mn contents obtained in fractions from the ABE profile. It was observed that the A_1 horizon showed the highest total Mn content in the fractions which were water-soluble, exchangeable, and bound to carbonates and to Fe-Mn oxides, and its amount decreased with depth in the fractions.

In the fraction bound to organic matter, the highest extraction was for the A_3 horizon, while in the residual fraction, a higher extraction was obtained for the A_2 horizon.

In the upper continental crust,[26] manganese presents a total content of 527.00 mg kg^{-1} soil. Taking this value as reference, it can be observed that the levels found in the sum of fractions are in agreement with this value.

The coefficient of variation for all fractions remained with high dispersion, ranging from 47.71% to 131.0%, showed the great variability of Mn among fractions and along of the soil profile.

The Mn levels in the residual fractions showed variations from 39.94% in the BA horizon to 81.81% in the A_1 horizon. These data were lower results obtained for Mn available from other sites of the ABE.[27,28] Among the non-residual fractions, the fraction bound to Fe-Mn oxides showed the highest Mn concentrations in the A_1, A_2, and A_3 horizons, while in the deeper AB, BA, and B horizons, major extractions occurred in fractions bound to the organic matter.

It can be inferred that in surface horizons, this element is available from Fe-Mn oxides, and with increasing depth in the ABE profile, manganese is most available from the organic matter.

Zinc

The result of the percentage distribution among the forms of zinc obtained in the ABE profile (Figure 5) indicates that this element was predominant in the residual fraction (F6) throughout the soil profile, with percentages ranging from 38.48% to 73.29%. Ma and Rao[19] found that the majority of zinc in the soil was associated with the residual fraction. This high Zn percentage in the residual fraction probably reflects the greater tendency of Zn to become unavailable in the soil.[19]

Table 5. Content of manganese (mg kg^{-1} ± SD[a]) extracted in each fraction of soil samples

	Soil profile					
Fraction	A1	A2	A3	AB	BA	B
Water soluble	1.33 ± 0.29	1.28 ± 0.14	0.80 ± 0.09	0.40 ± 0.01	0.41 ± 0.03	0.28 ± 0.02
Exchangeable	13.86 ± 0.36	< 0.05*	< 0.05*	< 0.05*	< 0.05*	< 0.05*
Carbonate	6.15 ± 0.02	3.82 ± 0.07	2.51 ± 0.17	1.05 ± 0.05	0.94 ± 0.07	0.69 ± 0.03
Fe-Mn oxide	48.51 ± 3.45	6.52 ± 0.27	28.94 ± 2.84	3.10 ± 0.17	1.41 ± 0.38	0.83 ± 0.03
Organic	0.79 ± 0.10	1.38 ± 0.14	10.68 ± 0.52	5.29 ± 0.14	3.49 ± 0.29	4.54 ± 0.03
Residual	15.70 ± 1.10	17.18 ± 0.29	12.64 ± 0.97	12.20 ± 1.14	9.40 ± 0.79	1.80 ± 0.14
Sum of all fractions	86.35	30.19	55.58	22.04	15.65	8.15
Non-residual / (%)	81.81	43.07	77.24	44.64	39.94	77.81
Residual / (%)	18.18	56.92	22.75	55.35	60.05	22.18

[a]SD = standard deviation (n = 3); *LOD (limit of detection) / (mg L^{-1}).

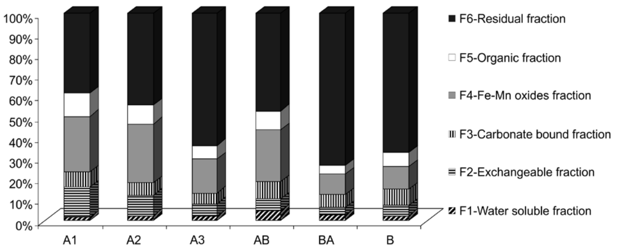

Figure 5. Percentage distribution of zinc in soil chemical fractions.

A considerable proportion of Zn in the soil profile (9.93 to 28.31%) was found in the fraction bound to Fe-Mn oxides (F4).

The contribution of organic matter (F5) to the Zn retention in the soil profile ranged from 4.37 to 11.24%, while the participation of forms which were associated with carbonate (F3), exchangeable (F2), and water-soluble (F1) ranged from 5.18 to 8.06%, 3.67 to 14.58%, and 1.46 to 4.69%, respectively. In relation to mobility and availability, Zn is highly available in the ABE profile, since over 12.00% of the total Zn was found in the sum of F1, F2, and F3. About the level of toxicity to plants, Zn levels obtained in the sum of fractions F1, F2, F3, F4, and F5 showed normal levels with the exception of the samples from the A$_1$ and A$_2$ surface horizons reach toxic levels (> 15 mg kg^{-1})[25] which can be harmful to plant growth.

Table 6 shows the Zn contents obtained in fractions from the ABE profile. It can be observed that the fractions which were soluble in water, bound to carbonates, bound to Fe-Mn oxides, and bound to organic matter showed a higher extraction in the A$_2$ horizon, while in the exchangeable and residual fractions, higher extractions were obtained in the A$_1$ and A$_3$ surface horizon, respectively. The Zn levels extracted in most fractions decreased with depth. The Zn levels obtained in the sum of the fractions are in agreement with the value of 52.00 mg kg^{-1} found in the upper continental crust.[26] The coefficient of variation for almost all fractions remained with high dispersion, ranging

Table 6. Content of zinc (mg kg^{-1} ± SD[a]) extracted in each fraction of soil samples

	Soil profile					
Fraction	A1	A2	A3	AB	BA	B
Water soluble	0.48 ± 0.06	0.97 ± 0.05	0.84 ± 0.05	0.76 ± 0.05	0.51 ± 0.08	0.39 ± 0.06
Exchangeable	4.86 ± 0.03	4.21 ± 0.10	2.58 ± 0.36	0.93 ± 0.11	0.78 ± 0.09	0.84 ± 0.11
Carbonate	2.38 ± 0.25	2.61 ± 0.19	2.21 ± 0.16	1.31 ± 0.08	1.34 ± 0.04	1.37 ± 0.03
Fe-Mn oxide	9.03 ± 0.36	12.05 ± 0.53	6.97 ± 0.53	4.10 ± 0.23	2.10 ± 0.26	1.92 ± 0.03
Organic	3.75 ± 0.16	3.87 ± 0.14	2.80 ± 0.27	1.48 ± 0.11	0.92 ± 0.06	1.23 ± 0.01
Residual	12.82 ± 5.35	18.86 ± 3.24	27.14 ± 4.95	7.66 ± 2.01	15.50 ± 0.76	11.68 ± 2.92
Sum of all fractions	33.32	42.57	42.57	16.25	21.15	17.43
Non-residual / (%)	61.51	55.68	36.16	52.81	26.71	33.00
Residual / (%)	38.48	44.31	63.83	47.18	73.29	66.99

[a]SD = standard deviation (n = 3); *LOD (limit of detection) / (mg L^{-1}).

from 31.80% to 76.92%, evidencing the great variability of Zn between fractions along the soil profile.

The Zn content present in non-residual fractions showed variations between 26.71% in the BA horizon and 61.52% in the A_1 horizon. This data showed the highest results for Zn available from other sites of the ABE.[27,28] Among the non-residual fractions, the fraction bound to Fe-Mn oxides obtained the highest Zn levels throughout the ABE profile. This may be due to the high constant stability of Zn oxides in soils.[18] Several studies have reported the dominance of Fe-Mn oxides bound to Zn .[11,12,19,22,23,35] It can be inferred that this element is preferentially available from Fe-Mn oxides.

Recovery

The recoveries of 4.00 mg L^{-1} Cu, 9.00 mg L^{-1} Fe, 2.00 mg L^{-1} Mn, and 1.00 mg L^{-1} Zn added in the fractions ranged from 80.30 to 95.50% for Cu, 90.20 to 96.50% for Fe, 83.70 to 103.70% for Mn, and from 89.20 to 104.20% for Zn.

Conclusions

The sequential extractions showed that the highest Cu, Fe, Mn, and Zn concentrations were found in the residual fraction for most samples and the sums of the non-residual fractions showed in appropriate levels for Cu, Fe and Mn, while Zn toxic levels presented in surface horizons. These data associated with high levels of organic matter show that this ABE soil profile investigated, still preserves its relative high fertility.

This study showed that the fractionation of elements found in the ABE profile has a similar behaviour, because among non-residual fractions, the fraction bound to Fe-Mn oxides was the most significant for the elements, except for Cu, which predominated in the fraction bound to organic compounds, and the exchangeable fraction was the least significant for the elements, except for Zn, which was less associated with the water-soluble fraction.

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