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Natural backgrounds and reference values of trace-element in earth murundus fields on the Southern Amazon

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ABSTRACT

Earth mounds fields are wetlands characterized by having a plan relief interspersed with mounds. The knowledge of the levels of trace elements in this environment is important to support sustainable management in areas subject to human intervention in order to reconcile the productive demand and environmental conservation. The objective of this study was to determine the levels and establishing baseline values for trace elements (Zn, Ni, Cu, Cr, Pb, As, Cd, and Se), Fe and Mn in the earth mounds fields soils on the southwest region of the Mato Grosso State. For this soil samples were collected at the depth of 0 to 20 and 20 to 40 cm in "murundus" and "flat" environments, which represent the mounds themselves and the area around it, respectively. The proposition of baseline values was performed according to Conama Resolution 420/2009. The baseline values proposed for these environments were: Zn 7.8; Ni 6.0; Cu 9.2; Cr 21.0; Pb 10.8; As 1.6; Cd <0.03; Se <0.31 and Mn 16.5 mg kg^{-1} and Fe 4.9 g kg^{-1}. The levels observed reflect the poverty of the source materials of these soils in these elements, as well as the absence of contamination.

Key words: wetlands; heavy metal; livestock; soil quality

Teores naturais e valores de referência de elementos-traço em campos de murundus na Amazônia Meridional

RESUMO

Campos de murundus são áreas úmidas caracterizadas por apresentar um relevo plano intermeados por montículos, denominados murundus. O conhecimento dos teores de elementos-traço nesses ambientes é importante para subsidiar uma gestão sustentável em áreas sujeitas à intervenção antrópica de modo conciliar a demanda produtiva e a conservação ambiental. O objetivo desse trabalho foi determinar os teores e propor valores de referência de qualidade (VRQs) de elementos-traço (Zn, Ni, Cu, Cr, Pb, As, Cd e Se), Fe e Mn no solo dos campos de murundus na região sudoeste de Mato Grosso, Brasil. Para isso, foram coletadas amostras de solo nas profundidades de 0 a 20 e 20 a 40 cm, nos ambientes "murundu" e "plano", os quais representam os murundus propriamente ditos e a área em seu entorno, respectivamente. A proposição de VRQs foi realizada de acordo com a resolução Conama 420/2009. Os VRQs propostos para esses ambientes foram: Zn 7,8; Ni 6,0; Cu 9,2; Cr 21,0; Pb 10,8; As 1,6; Cd <0,03, Se <0,31 e Mn 16,5 mg kg^{-1} e Fe 4,9 g kg^{-1}. Os teores observados refletem a pobreza do material de origem dos solos nesses elementos, bem como a ausência de contaminação.

Palavras-chave: áreas úmidas; metal pesado; pecuária; qualidade do solo

Introduction

The knowledge of trace element contents in the soil represents an important tool to assist the management of natural or anthropic areas, either for environmental monitoring, recovery of contaminated environments or for proper use and occupation (Conama, 2009; Ajmone-Marsan & Biasioli, 2010; Jarva et al., 2010; Alcântara et al., 2011; Chapman, 2012; Almeida et al., 2016).

Brazilian environmental legislation through the National Environmental Council (Conama) recommends that each state establishes its quality reference values (QRVs), taking the environmental variations of each region into account (Conama, 2009). Some Brazilian states already have QRVs stipulated, such as Minas Gerais (Copam, 2011), São Paulo (Cetesb, 2005), Rio Grande do Sul (Fepam, 2014), Paraíba (Copam, 2014; Almeida et al., 2016) and Pernambuco (CPRH, 2014) and other studies on the concentration of these elements in the soil have been conducted in other Brazilian regions (Pierangeli et al., 2009; Fadigas et al., 2010; Paye et al., 2012; Santos & Alleoni, 2013; Pierangeli et al., 2015).

QRVs of trace elements in soils have not yet been established for the State of Mato Grosso, for which only a few sparse studies on trace elements have been conducted (Pierangeli et al., 2009; Alcântara et al., 2011; Santos & Alleoni, 2013). However, due to its vast territory, high diversity of soils and landscapes (Moreira & Vasconcelos, 2007) and occurrence of three major biomes, namely the Amazonia, Pantanal and Cerrado, the natural trace element contents in the different ecosystems need to be determined in order to establish the QRVs for the state.

Murundus fields (seasonally flooded gramineous fields with scattered mounds) are important in this context, as they are common in the Brazilian landscape and widely spread in Mato Grosso lands. Drainage is restricted murundus fields. What are the natural trace element contents in these environments? In order to answer this question, this work aimed to determine the levels and propose QRVs for Fe, Mn, Zn, Ni, Cu, Cr, Pb, As, Cd and Se in murundus field soils located in the Guaporé river basin, southwest region of the State of Mato Grosso.

Material and Methods

The murundus fields studied cover a region between the municipalities of Pontes and Lacerda and Vila Bela da Santíssima Trindade, southwest of the State of Mato Grosso (Figure 1), extending beyond the Brazil-Bolivia border, and occupying approximately 5,500 km². A more detailed description of this area is presented by Santos et al. (2015).

Conama Resolution 420/2009 recommends that QRVs be determined in areas without anthropogenic interference. However, this region is used for extensive cattle ranching, apparently without the use of agricultural pesticides. Mining activities did not occur in the sampling areas. Some properties have incorporated planted pastures, soil plowing, drainage channels due to seasonal rainfall and the use of fires. However, areas with the minimum interference possible were selected for sample collection.

In order to determine trace element levels, soil samples were collected in these murundus fields during October and November 2011. Plintossolos, Cambisols and Neosols occur in these fields. In order to sample the most varied classes of soils in the study region, four sampling areas were selected, shown in Figure 1. In each sampling area, 36 samples were collected within a 20 km radius: 18 samples in the "flat" environment (area around the murundu) and 18 samples in the "murundu" environment, at 0 to 20 cm depth, and at 20 to 40 cm depth, totaling 144 samples.

The following trace elements were analyzed: Zn, Ni, Cu, Cr, Pb, As, Cd e Se, besides Fe and Mn. For the extraction of these elements from the soil samples, the Usepa 3051A methodology recommended by the US Environmental Protection Agency (Usepa, 2007) and recommended by Conama Resolution 420/2009 (Conama, 2009) was used. Fe, Mn and Zn were determined by flame atomic absorption spectrometry, while Cu, Ni, Cd, Pb, As and Si were determined by graphite furnace atomic absorption spectrometry. Quality control was established with a certified reference sample (Montana L. Soil 2710A). Trace element recoveries are shown in table 1. The detection limit of the method was obtained by the following equation: ["White" sample mean + (3 × standard deviation)].

Outliers in the data set of the analyzed elements were identified and removed by the Grubbs method. The Shapiro-Wilk normality test was used to check data distribution. Descriptive statisticts and Mann-Whitney U test were used to compare the environments ("flat" and "murundu" areas) and depths (0-20 and 20-40 cm), as data had a non-normal distribution.

In order to establish the QRVs for trace elements analyzed in these environments, the methodology defined in the Conama Resolution 420/2009 (Conama, 2009) was followed, using only the samples collected at 0 to 20 cm depths. All statistical tests were performed in the Xlstat software (Addinsoft, 2013).

Results and Discussion

The descriptive analysis of the studied elements is presented in table 2. It was observed that data had an overall wide amplitude and high coefficient of variation, which in fact was expected considering that these were environmental samples and that the sampling procedure had as a goal to identify the most varied differences within this ecosystem.

There was a low standard deviation, with values mostly scattered below 4 units in relation to the average, except for Cr and Mn. This shows that variability of the content of each element is low within the same environment.

Based on the Mann-Whitney U test ($p < 0.05$), only Fe, Mn and Pb showed significant differences between the "murundu" and "flat" environments, with higher contents in the "flat" environment

Fe and Mn are very susceptible to oxidative conditions, typical of murundus fields, being the main donors of electrons in the lack of oxygen, and becoming free in the soil solution in their reduced form (Fe^{2+} and Mn^{2+}), what make them easily leached out (Kerr et al., 2008; Laing et al., 2009). The flat area surrounding the murundu presented higher Fe contents than the

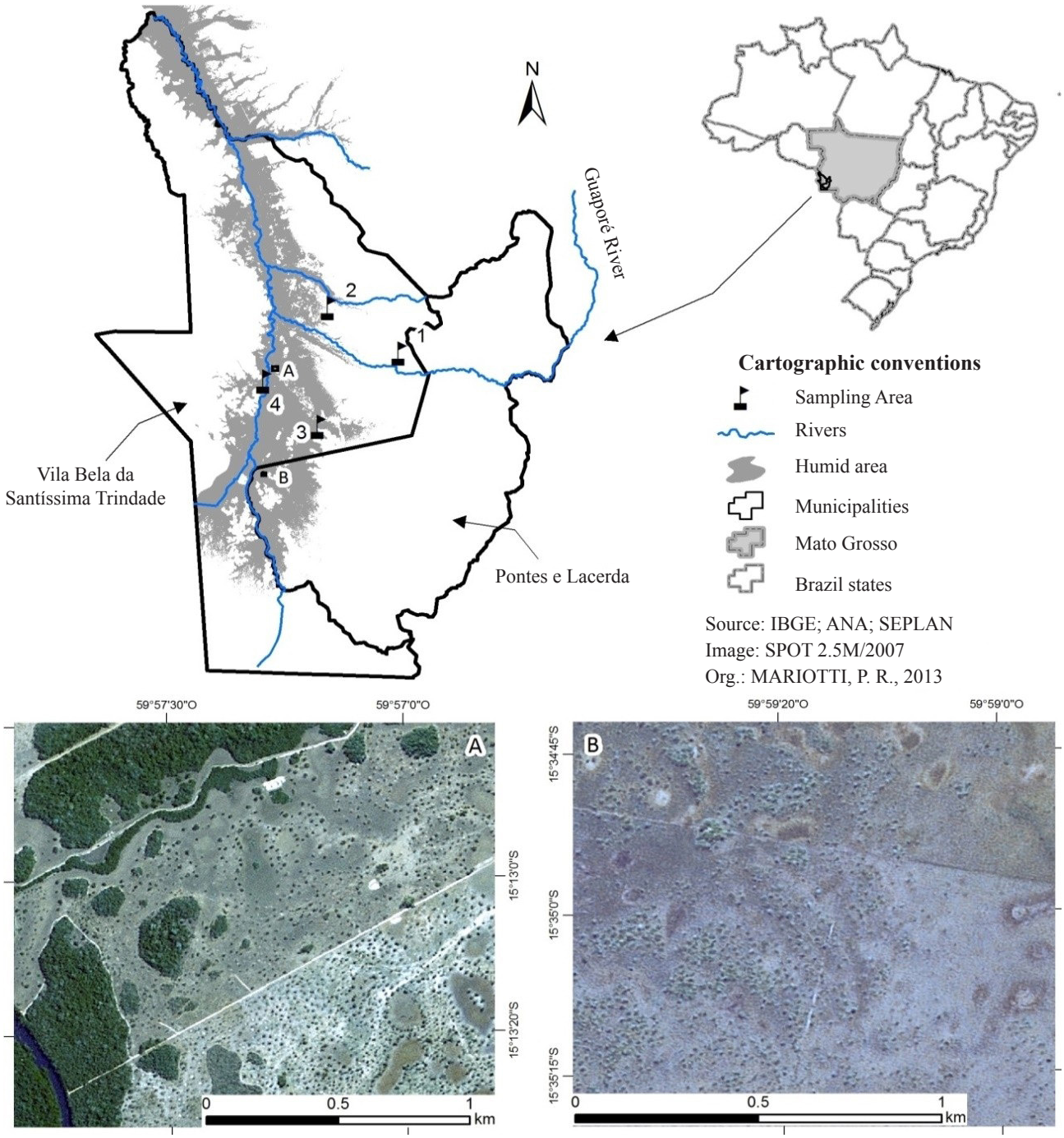

Figure 1. Location of the study area. Satellite images (A and B) of the murundus fields of the Guaporé River basin, Southern Amazonia. Soil sampling areas (1, 2, 3 and 4).

Table 1. Recovery and detection limit (DL) of the methods employed to determine trace elements, Fe and Mn of murundus fields in the Guaporé River basin, Southern Amazonia.

Element	Recovery (%)	DL[1] (mg kg^{-1})
Fe	77	7.24
Mn	86	0.70
Zn	84	1.40
Ni	72	0.20
Cu	75	0.31
Cr	48	0.57
Pb	58	0.21
As	94	0.08
Cd	105	0.03
Se	65	0.31

1 - Detection Limit.

murundu. Even though murundu fields are not flooded during the rainy season, Fe and Mn may laterally leach or migrate from the "murundu" to the "flat" environment, thus decreasing the contents of these elements in the former, what may explain the differences observed in this study. Fe content in the soil derives from both the source material and the soil formation processes, being higher in soils derived from mafic rocks. Fe levels in the soils of these murundus fields can be considered low, since according to Kabata-Pendias & Pendias (2001), soil Fe content vary from 5 to 50 g kg^{-1}.

Pb contents were higher in the flat area in relation to the murundu. The literature points that Pb presents little mobility

Table 2. Descriptive statistics of trace element, Fe and Mn contents in the soil (0-20 cm) and comparison between environments ("flat" and "murundu") of murundus fields in the Guaporé River basin, Southern Amazonia.

Environment	Statistic	Fe	Mn	Zn	Ni	Cu	Cr	Pb	As	Cd[1]	Se[1]
		g kg^{-1}	mg kg^{-1}								
Murundu	Minimum	0.6	1.7	1.6	0.5	1.0	2.2	1.9	0.0	0.03	0.3
	Maximum	4.7	21.9	16.9	9.4	11.9	31.9	10.6	1.6	0.03	0.3
	Medium	2.4	4.3	3.2	2.5	3.3	8.2	3.4	0.7	0.03	0.3
	Average	2.5	4.9	4.2	2.8	4.1	10.4	4.8	0.7	0.03	0.3
	CV (%)	40	51	81	80	70	64	56	67	-	-
	DP	1.0	2.5	3.4	2.3	2.9	6.7	2.7	0.4	-	-
Flat	Minimum	2.0	2.1	1.4	0.9	1.6	4.2	2.1	0.1	0.03	0.3
	Maximum	5.7	35.6	12.7	6.0	9.7	25.4	12.7	1.7	0.03	0.3
	Medium	3.4	6.9	3.9	2.6	3.9	8.9	7.0	0.9	0.03	0.3
	Average	3.5	8.8	4.6	2.9	4.6	10.5	7.0	0.9	0.03	0.3
	CV (%)	31	87	54	58	46	48	37	55	-	-
	DP	1.1	7.5	2.5	1.7	2.1	5.0	2.6	0.5	-	-
p-valor[2]		<0,01	0.01	0.08	0.40	0.14	0.29	<0.01	0.10	-	-

1 - Values corresponding to the detection limit of the method (Table 1); 2 - Mann-Whitney U test ($p < 0.05$) for the Murundu and Flat environment factors.

in the soil, being strongly adsorbed to clay minerals and Fe and Mn oxides and complexed by soil organic matter (Kabata-Pendias & Pendias, 2001). Thus, Pb may be accumulating in the flat environment during flooding, becoming part of the composition of secondary minerals or complexed to organic matter in the soil. It was observed that Pb contents were lower than those reported in the literature for other soils (Pierangeli et al., 2009; Santos & Alleoni, 2013; Pierangeli et al., 2015). This fact may be related to the soil granulometry of these murundus fields: 200 and 250 g of kg^{-1} of clay in the flat and murundu area, respectively (Santos et al., 2015).

The observed values of Cd and Si were lower than the DL of the method. Thus, the results of these elements are presented as equal to the DL, as recommended by Conama Resolution 420/2009 (Conama, 2009).

The contents of the evaluated elements within each depth interval (0-20 and 20-40 cm) in the "murundu" and "flat" environments are presented in figures 2 and 3, respectively.

In the "murundu" environment (Figure 2), Fe content was different between the two depths, with higher values at 20-40 cm, indicating that reduction and leaching of Fe to deeper layers or to the "flat" environment occurs even in this environment. As for the other elements, no differences were observed between depths in this environment. This gives evidence of higher leaching susceptibility of Fe in a reducing environment.

In the "flat" environment (Figure 3), Mn contents were higher in the superficial layer (0-20 cm). However, the content of the other elements were equal between the depths in this environment. The behavior of Mn in the soil is very complex and dependend on many environmental conditions, especially pH and oxy-reduction potential (Eh) (Kabata-Pendias & Pendias, 2001). According to Sousa et al. (2009), under conditions of oxidation and seasonal reduction, Mn oxides may form co-precipitates, solid solutions and, perhaps, superstructures with Fe oxides. Thus, Mn could concentrate on the surface layer of flooded soil during the rainy season.

The QRVs (Table 3) for the trace elements studied here were proposed considering the 90th percentile of the data set, because the 75th percentile is even more restrictive (Paye

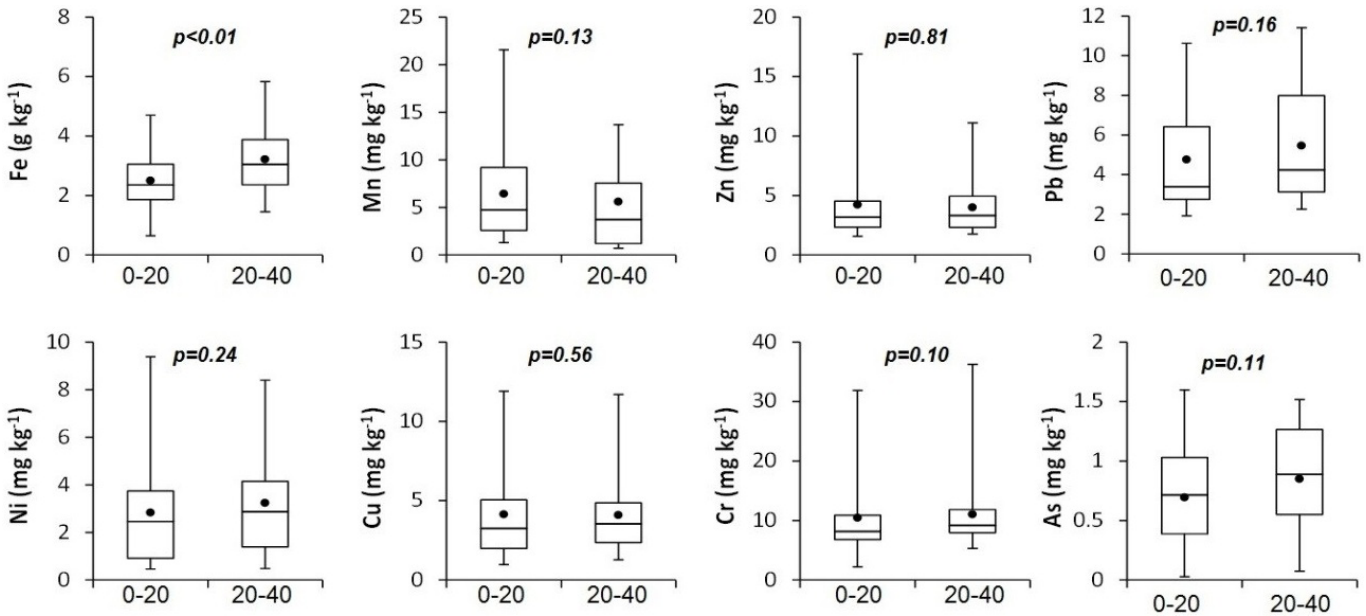

Figure 2. Fe and Mn contents at 0-20 and 20-40 cm soil depth in the "murundu" environment of murundus fields in the Guaporé River basin, Southern Amazonia. Mann-Whitney U test ($p < 0.05$).

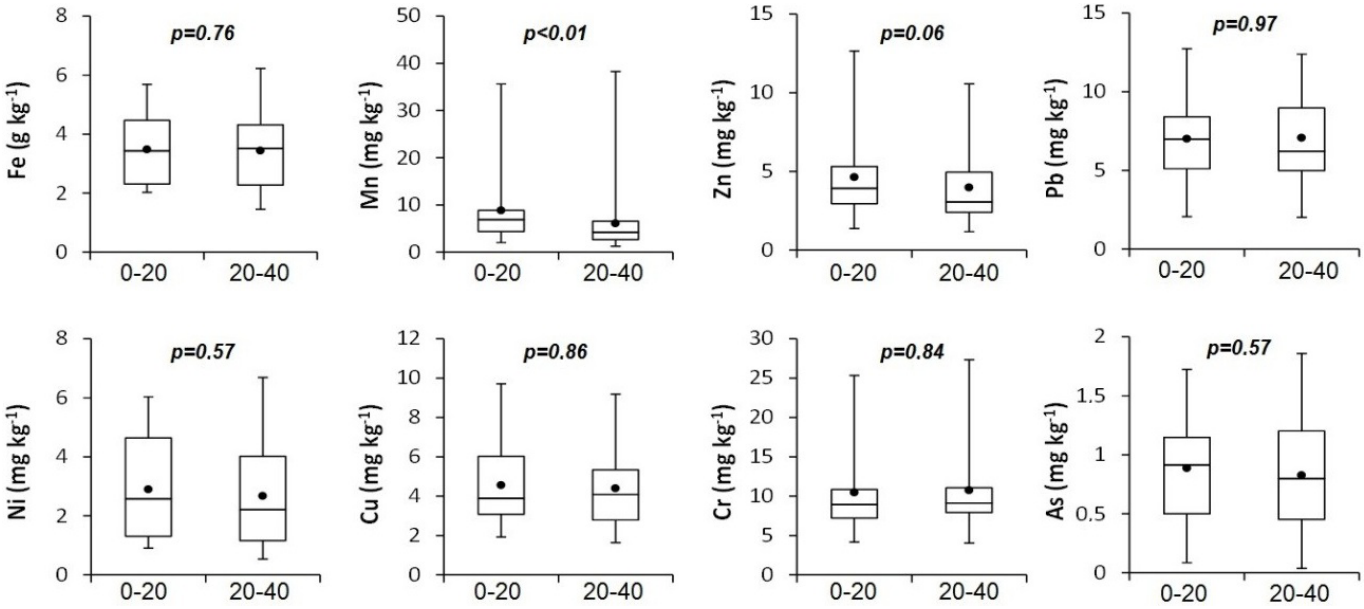

Figure 3. Fe and Mn contents at 0-20 and 20-40 cm soil depth in the "flat" environment of murundus fields in the Guaporé River basin, Southern Amazonia. Mann-Whitney U test ($p < 0.05$).

et al., 2012). Note that the QRVs established for the "flat" and "murundu" environments are similar to each other and mostly lower than the QRVs determined for other Brazilian regions (Table 3). The low levels of trace elements observed here reflect the source material. These are soils formed from unconsolidated sediments of the Guaporé Formation (Santos et al., 2015), in addition to leaching processes favored by the solubility of the elements (Olivie-Lauquet et al., 2001), which may further decrease the natural levels of these elements in these soils.

Pierangeli et. al (2015) presented mean values of several elements in native vegetation soils in the state of Mato Grosso. They showed higher values than those observed in the present study (Table 2) for the following analyzed elements: Mn 42.37; Zn 8.35; Cu 7.69; Cr 31.46; Pb 11.8; As 4.43 mg kg^{-1}. This shows the need to establish stratified QRVs for the state, a situation that is also foreseen in Conama Resolution 420/2009 (Conama, 2009). Such stratification of QRVs within state boundaries has been similarly applied in the Rio Grande do Sul (Fepam, 2014), where QRVs were investigated in 5 soil groups originating from different geomorphological/geological provinces of the state.

The Conama Resolution 420/2009 (Conama, 2009) still establishes prevention values (PV), which are threshold values of the concentration of certain elements in the soil that guarantee the maintenance of soil functionality or, in a corrective way, restore their quality or recover it in a manner compatible with the intended uses. In this perspective, it is important to observe that Cr was proportionally the closest element to the prevention value, representing 28% of the established value, while Cd, on the other hand, represents 2.3%, the farthest from the PV. In all cases, the trace elements analyzed did not represent 1/3 of the PV established by current legislation.

The literature in general addresses the impacts of anthropization as activities that compromise the integrity of natural environments. These changes, in the case of trace elements, may promote environmental contamination (Ajmone-Marsan & Biasioli, 2010; Alcântara et al., 2011; Luo et al., 2012). When considering the low values of trace elements and Fe found for these environments in the present study, it

Table 3. Quality reference values (QRVs) proposed for soils of "murundu" and "flat" (0-20 cm) environments of murundus fields in the Guaporé River basin, Southern Amazonia.

ET	Murundu		n	Flat		n	Copam,	Cetesb,	Fepam,	CPRH,	Copam,	PV[2]
(mg kg^{-1})	P90[3]	%[4]	-	P90[3]	%[4]	-	2011	2005	2014[1]	2014	2014	
Fe[5]	4.2	-	36	4.9	-	36	-	-	-	-	-	-
Mn	8.4	-	35	16.5	-	31	-	-	-	-	-	-
Zn	7.6	2.6	36	7.8	2.5	36	46.5	60	29	35	33.65	300
Ni	6.0	20	36	5.4	18	36	21.5	13	7	9	14.44	30
Cu	9.2	15	36	7.8	13	36	49	35	11	5	20.82	60
Cr	21	28	36	19.5	26	36	75	40	21	35	48.35	75
Pb	8.8	12	34	10.8	15	36	19.5	17	16	13	14.62	72
As	1.2	8	36	1.6	10.7	36	8	3.5	-	0.6	-	15
Cd[6]	<0.03	2.3	-	<0.03	2.3	-	<0.04	<0.05	0.42	0.5	0.08	1.3
Se[6]	<0.31	6.2	-	<0.31	6.2	-	0.5	0.25	-	0.4	-	5

1 - Sandstone sedimentary rocks of the Plateau, of the Rio Grande do Sul Shield and the Peripheral Depression; 2 - Prevention Values (Conama, 2009); 3 - Cutting of the data set at the 90th percentile; 4 - Proportion in relation to PV, obtained by the following equation [% = ET (P90)×100 / PV.]; 5 - Data shown in g kg^{-1}; 6- QRVs considering the DL (Table 1).

should be assumed that the balance of these environments may become compromised if these elements exceed the QRVs proposed here. It is also necessary to calculate local prevention values because murundus fields are key areas for water purification, recharge of aquifers and maintenance of various environmental services.

Conclusions

The studied elements showed no difference between the "murundu" and "flat" environments, except for Mn and Pb that were higher in the "flat" environment.

Mn contents were higher in the 0 to 20 cm layer of the "flat" environment.

The proposed QRVs for these environments were: Zn 7.8; Ni 6.0; Cu 9.2; Cr 21.0; Pb 10.8; As 1.6; Cd < 0.03; Se < 0.31 and Mn 16.5 mg kg^{-1} and Fe 4.9 g kg^{-1}, which were considered low in relation to the QRVs established for soils of other regions.

In view of the high geobiodiversity of Mato Grosso, similar studies must be conducted in the cerrado, pantanal and amazonian environments in order to establish QRVs for the state, considering regional specificities.

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