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Assessment of Trace Element Contents in Soils and Water from Cerrado Wetlands, Triângulo Mineiro Region

Bruno Teixeira Ribeiro[(1)*], Diogo Costa Nascimento[(2)], Nilton Curi[(1)], Luiz Roberto Guimarães Guilherme[(3)], Enio Tarso de Souza Costa[(2)], Guilherme Lopes[(1)] and João Paulo Carneiro[(3)]

[(1)] Universidade Federal de Lavras, Departamento de Ciência do Solo, Lavras, Minas Gerais, Brasil.
[(2)] Universidade Federal de Uberlândia, Instituto de Ciências Agrárias, Uberlândia, Minas Gerais, Brasil.
[(3)] Universidade Federal de Lavras, Departamento de Ciência do Solo, Programa de Pós-Graduação em Ciência do Solo, Lavras, Minas Gerais, Brasil.

ABSTRACT: In the Brazilian Cerrado biome, there are wetlands locally known as "Veredas", which are swampy plains between hills and rivers. Since the 1970's, the Cerrado biome has been gradually converted to livestock, crop, or forestry production. Until now, very few studies were conducted to evaluate the baseline contents of trace elements in Cerrado wetland soils. Due to their position in the landscape (bottom lands), the wetlands are potentially susceptible to contamination by runoff and/or leaching from surrounding areas at higher altitudes. This work evaluated the As, Cd, Pb, Ni, Zn, Cu, Mn, and Fe contents in soils from six wetlands (undisturbed and disturbed) in the Minas Gerais Triangle region, Brazil. In each wetland, we collected topsoil samples (0.00-0.20 m layer) and subsurface samples (0.40-0.70 m layer) at different landscape positions in the wetlands (upper, middle, and bottom positions). The soil samples were air-dried, ground, and sieved through 2-mm mesh. Afterwards, the soil digestion was performed according to the USEPA 3051A protocol, and the trace elements were determined by atomic absorption spectrometry (flame or graphite furnace atomization). Water samples were also collected monthly from September 2014 to September 2015 to determine the elemental composition by inductively coupled plasma optical emission spectrometry. The contents of all soil trace elements studied were below the threshold values established by Brazilian guidelines. The soil trace element (cations and/or oxyanions) distributions varied according to soil depth and organic matter content. Our findings contribute to the sparse inventory of Brazilian Cerrado wetlands regarding trace-element contents.

Keywords: waterlogged soils, soil contamination, tropical soils, heavy metals.

*** Corresponding author:**
E-mail: brunoribeiro@ufla.br

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INTRODUCTION

The Brazilian Cerrado is the second largest biome in Brazil (after the Amazon), with an area of 2 million km^2 (~24 % of Brazilian land surface), and contributing to five important watersheds. Since the 1970's, the Cerrado biome has been gradually converted to crop, livestock, or forestry production. It is estimated that almost 50 % of native vegetation has been cleared (Klink and Machado, 2005). Undoubtedly, the exploration of the Brazilian Cerrado for agricultural production is considered one of the greatest successes of worldwide agricultural science in the 20th century (Lopes and Guilherme, 2016). For this reason, Brazil is currently recognized worldwide for its food production potential. However, the environmental consequences of the Cerrado's transformation were not satisfactorily assessed (Grecchi et al., 2014).

In the Cerrado biome, there are wetland areas (named "Veredas" from the Latin *veredus*) that are characterized by waterlogged soils with relatively stable water levels and *Mauritis flexuosa* L.f. palm forests (Junk et al., 2014). It is estimated that 20 % of Brazilian land surface is covered by wetlands (including the Pantanal and Amazon floodplains) (Junk et al., 2011).

Cerrado wetlands play extremely important ecosystem services (Junk, 2013; Rosolen et al., 2015a; Hu et al., 2017), such as: 1) water springs, 2) groundwater recharge, 3) carbon storage, and 4) wildlife habitat. Due to their position in the landscape (depressions on the flat plateau), the wetlands may be susceptible to contamination by agrochemicals through runoff and/or leaching from surrounding areas at higher altitudes (Rosolen et al., 2015b). Despite the environmental importance of Cerrado wetlands, there is no national policy that efficiently regulates their protection. As of the last edition of the Brazilian Forest Code in 2012 (Alencar, 2016), Cerrado wetlands have been considered permanent and priority areas for environmental protection (Rosolen et al., 2015a). They function as the drainage line for the Cerrado biome.

Despite the fact that Brazil signed the Ramsar Convention in 1993, a minimal effort has been given to the Cerrado wetlands inventory, mainly in the Cerrado biome. There are very few studies assessing the background contents of trace elements and their potential contamination of wetland soils from the Cerrado region. In the north part of the Minas Gerais State, Moraes and Horn (2010) found high contents of Cd and Cr. More recently, the As, Cr, and Cu contents found in five wetlands in the Minas Gerais Triangle region exceed the threshold values established by Brazilian guidelines (Rosolen et al., 2015b). The contamination of wetland may be related to land-use change, as has also been observed for other wetlands worldwide (Nabulo et al., 2008; Bai et al., 2010). In Brazil, the threshold values are regulated by the Environmental National Council (Conama Resolution 420/2009), the Environmental Company of São Paulo State (Cetesb, 2014), and by the Environmental Foundation of Minas Gerais State (Copam Normative Deliberation 166/2011).

Thus, considering the substantial lack of information about trace-element baseline contents in Cerrado wetland soils, this work was carried out to assess the As, Cd, Pb, Ni, Zn, Cu, Mn, and Fe contents in wetlands (disturbed and undisturbed) in the Triângulo Mineiro region, Brazil. The contents of these elements were correlated to clay content, soil organic matter, and its fractions (C-fulvic acid, C-humic acid, and C-humin), as well as to the soil cation exchange capacity. In addition, the elemental composition of water from Cerrado wetlands was determined. This study contributes to the information about elemental contents in waterlogged soils of the Brazilian Cerrado biome.

MATERIALS AND METHODS

Area description and soil sampling

Six wetlands, herein labeled as W1, W2, W3, W4, W5, and W6, near Uberlândia, Minas Gerais State, Brazil, were selected for this study (Figure 1). The climate is Aw (Köppen's

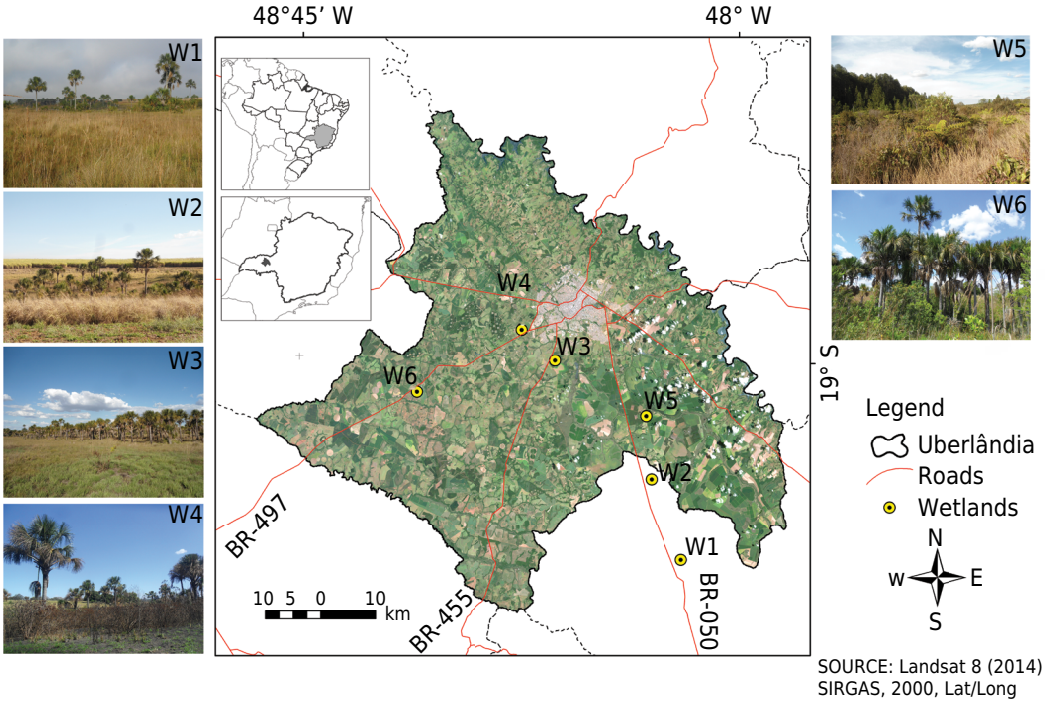

Figure 1. Location and overview of selected wetlands (W1, W2, W3, W4, W5, and W6), Uberlândia region, Minas Gerais State, Brazil. The palm *Mauritis flexuosa* L.f. can be seen in W1, W2, W3, W4, and W6 wetland areas.

classification system), and the total annual average rainfall is 1,472 mm, which is distributed in two distinct periods: spring-summer or wet season (86 % of total annual rainfall) and fall-winter or dry season (14 % of total annual rainfall) (Ribeiro et al., 2013). The altitudes of the wetlands ranged from 745-892 m a.s.l. The geology is characterized by sedimentary deposits, including clay sediments (locally known as the "Chapada" Plateau surface) and sandstones of the Bauru Group (Nishiyama, 1989; Ramos et al., 2006).

In each wetland, three transects (T1, T2, and T3) from non-hydromorphic to hydromorphic landscape portion were established (Figure 2). On the hydromorphic portion, each transect was divided into upper, middle, and bottom positions. Composite soil samples were collected from 0.00-0.20 and 0.40-0.70 m layers at the upper, middle, and bottom positions in each transect. Each transect was considered a field replicate. Each composite sample was composed by mixing four single samples collected around (~1.0 m) from the central point (Figure 2). In addition, soil samples were collected at the same layers in the non-hydromorphic portion (P1 position). According to the Brazilian System of Soil Classification (Santos et al., 2018), *Latossolo Vermelho Distrófico* occurs in the P1 position (Hapludox or Ferralsols, according to Soil Taxonomy and FAO, respectively). Inside the hydromorphic portion, *Gleissolo Háplico* occurred in the upper position, and *Gleissolo Melânico* occurred in the middle and bottom positions. These soils corresponded to Entisols and Gleysols, according to Soil Taxonomy and FAO, respectively. The soils in the hydromorphic portion were permanently or seasonally waterlogged (Nascimento et al., 2018). The wetland soils were covered mainly by plants of the Poaceae, Asteraceae, Arecaceae, Cyperaceae, Melastomataceae, and Fabaceae families (Araújo et al., 2002). *Mauritis flexuosa* L.f. is a typical indicator plant of wetland soils in the Brazilian Cerrado biome (Figure 1). The W1 and W4 wetlands were surrounded by annual crops (mainly corn). The W2 and W6 wetlands were surrounded by sugarcane fields; and the W3 and W5 wetlands were surrounded by typical Cerrado vegetation. The W1, W2, W4, and W6 were considered disturbed wetlands, while W3 and W5 were considered undisturbed wetlands.

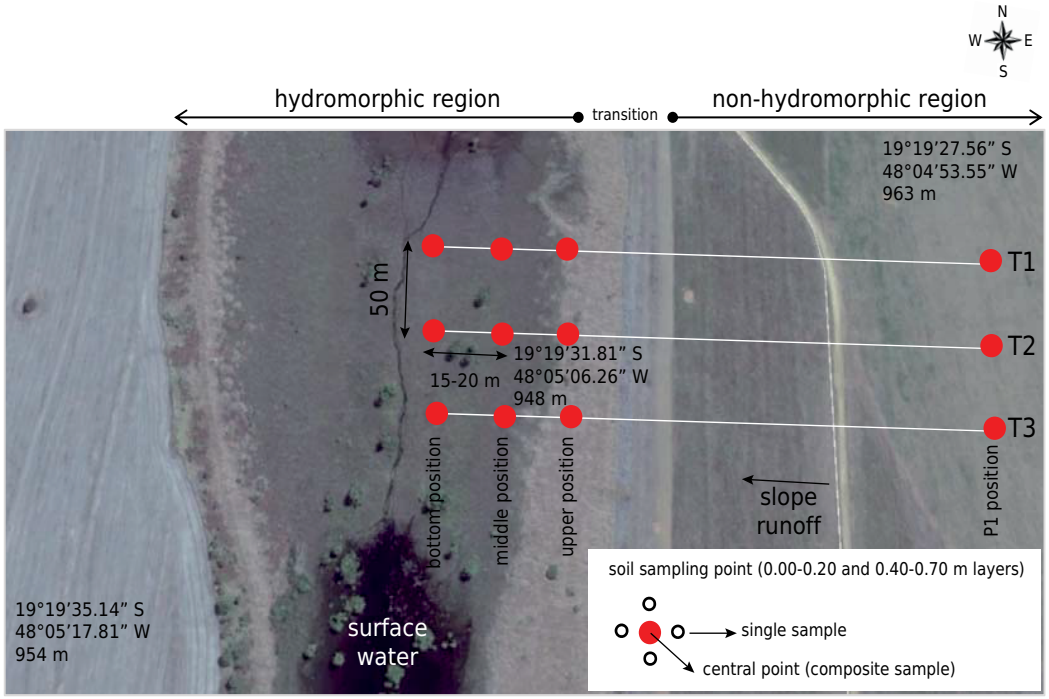

Figure 2. Details of soil sampling scheme. The background image was obtained from Google Earth and it corresponds to the W1 wetland area.

Preparation and characterization of soil samples

After fieldwork, the soil samples were air-dried, passed through a 2-mm sieve, and stored in plastic bags for further characterization. The particle size distribution was determined by the pipette method (Day, 1965) after dispensing 10 g of soil into a 250-mL glass beaker, containing 190 mL of distilled water plus 10 mL of NaOH 1 mol L^{-1}. For complete dispersion, the soil suspension was sonicated (output power = 80 W) using a probe (19 mm diameter inserted at 2.5 cm) for 300 s. The soil organic matter (SOM) was determined by the Walkley and Black method. Soil organic matter fractions (C-fulvic acid, C-humic acid, and C-humin) were obtained according to Nelson and Sommers (1982). The soil pH was determined in distilled water (soil-water ratio of 1:2.5). The effective cation exchange capacity (CEC) was determined by the sum of exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+}, and Al^{3+}). Exchangle Ca, Mg, and Al were extracted with a KCl 1.0 mol L^{-1} solution, and K^{+} was extracted with Mehlich-1 solution. Exchangeble Ca and Mg were quantified using a flame atomic absorption spectrometer (FAAS). Exchangeble K was quantified using a flame photometer, and Al^{3+} was quantified by titration with a NaOH 0.025 mol L^{-1} solution. All determinations were made in three lab replicates and complete details of analytical procedures can be found in Teixeira et al. (2017). The soil properties are in table 1.

The clay fraction of soils was dominated by kaolinite followed by gibbsite, and was determined by X-ray diffraction analysis, using a Siemens D5000 diffractometer, powder method, CoKα radiation, Fe filter, and 4-52° range.

Soil digestion and trace-elements determination

Homogeneous portions of the air-dried soil samples were passed through a 2 mm sieve, thoroughly ground using an agate mortar, and passed through a 150-µm nylon mesh. Sub-samples (1.0 g) was added into 50-mL Teflon® PTFE vessels containing 10 mL of HNO_3 (Sigma-Aldrich®). The soil samples were microwave-digested according to the USEPA Method 3051A (USEPA, 1998). After digestion, the samples were filtered (Whatmann No. 40 filter paper) by rinsing with 10 mL of ultrapure water. The As, Cd,

Table 1. Some properties of soils selected for the study

Wetland	Position	pH(H_2O)	Clay	Sand	Silt	TOC	C-fulvic acid	C-humic acid	C-humin
			g kg^{-1}						
			0.00-0.20 m layer						
1	P1	5.4	825	128	47	24.2	5.06	2.11	10.87
	Upper	4.9	751	194	56	23.8	6.06	2.99	12.17
	Middle	5.2	755	182	63	51.2	10.69	9.89	21.49
	Bottom	5.4	402	341	257	125.9	15.09	13.84	30.00
2	P1	5.7	288	676	36	19.3	3.02	0.64	6.71
	Upper	5.5	291	671	39	26.9	4.68	5.68	10.32
	Middle	4.5	317	626	57	49.5	6.50	8.53	18.13
	Bottom	4.4	308	501	192	137.5	11.04	9.81	23.34
3	P1	5.3	333	637	31	12.6	6.19	0.74	3.85
	Upper	4.2	149	831	20	18.4	3.74	2.08	6.30
	Middle	4.3	227	717	57	62.1	6.79	12.48	15.29
	Bottom	4.1	224	511	265	119.8	13.10	14.01	30.00
4	P1	6.1	367	570	62	19.9	4.00	1.12	8.05
	Upper	5.5	303	656	41	24.0	4.71	2.69	6.06
	Middle	4.7	440	508	52	45.4	7.13	8.65	8.34
	Bottom	4.4	474	414	113	94.1	11.99	14.09	17.38
5	P1	4.9	799	194	8	19.3	6.33	1.93	9.78
	Upper	4.6	700	288	12	22.6	6.71	2.84	10.37
	Middle	4.6	865	113	22	48.5	9.87	14.25	13.94
	Bottom	4.5	676	226	98	55.7	13.21	14.25	28.41
6	P1	5.4	156	818	26	13.5	5.84	2.50	4.93
	Upper	5.1	138	827	35	15.9	6.59	2.42	7.40
	Middle	4.6	280	633	87	46.4	8.67	7.70	9.24
	Bottom	5.0	407	386	207	91.8	12.24	14.57	30.00
			0.40-0.70 m layer						
1	P1	4.7	863	126	10	16.0	7.44	4.21	9.28
	Upper	5.4	821	169	10	8.7	5.89	2.42	5.72
	Middle	5.2	819	166	15	7.9	6.40	2.28	5.13
	Bottom	4.6	765	188	47	51.6	8.90	14.57	16.09
2	P1	5.4	324	662	14	12.2	4.97	1.56	6.05
	Upper	5.0	233	748	19	4.2	2.35	1.70	2.18
	Middle	4.9	223	743	34	15.7	1.70	1.34	2.94
	Bottom	4.6	410	531	59	99.2	6.73	14.57	30.00
3	P1	4.8	372	616	12	5.0	2.43	1.27	3.80
	Upper	5.1	173	790	37	4.1	2.31	1.60	2.66
	Middle	5.1	139	840	21	4.8	2.40	1.89	2.37
	Bottom	4.9	176	779	45	28.2	3.77	10.52	13.62
4	P1	5.7	430	543	27	15.9	1.32	1.16	4.94
	Upper	5.2	326	641	33	6.4	1.67	1.48	4.22
	Middle	4.8	402	539	59	41.4	5.11	14.43	16.19
	Bottom	5.0	531	399	70	126.6	9.89	14.57	27.91
5	P1	4.9	815	164	22	11.4	1.67	1.41	5.79
	Upper	5.4	666	320	14	50.3	2.54	1.16	7.03
	Middle	4.4	715	220	65	42.1	6.19	9.19	17.56
	Bottom	4.6	549	308	144	123.2	13.61	14.57	29.34
6	P1	5.9	172	787	41	6.8	0.82	0.80	3.99
	Upper	5.0	160	804	36	5.4	0.61	0.83	2.75
	Middle	4.8	201	755	44	32.9	1.04	8.17	5.22
	Bottom	4.5	500	407	93	49.7	4.21	14.57	15.47

P1 = non-hydromorphic portion; TOC = total organic carbon; pH in water (soil:water ratio of 1:2.5); clay, silt, and sand contents according to Pipette Method (Day, 1965); TOC, C-fulvic acid, C-humic acid, and C-humin according to Nelson and Sommers (1982).

Pb, and Ni concentrations were determined using a graphite-furnace atomic absorption spectrometer (GFAAS). The Zn, Cu, Mn, and Fe concentrations were determined using a flame atomic absorption spectrometer (FAAS). The metal concentration determinations were performed using an absorption atomic spectrometer PerkinElmer AAnalysit™ 800 with either flame (FAAS) or graphite furnace (GAAS) atomization modules. Total Flow™ gas controls for FAAS analysis and a transversely heated graphite Furnace (THGA) with longitudinal Zeeman-effect background corrector were used. The selected wavelengths (nm) were: As (197.3), Cd (228.8), Pb (217.0), Ni (232.0), Zn (213.9), Cu (324.7), Mn (279.5), and Fe (248.3). More details of this spectrometric analysis can be found in Penha et al. (2017).

In order to verify the accuracy of the digestion of each batch, blank samples and the Standard Reference Material® 2710A (Montana I Soil) were used. The detection limits (DL) were determined by equation 1 (Apha, 1989):

$$DL_e = \bar{X} + (\sigma.t) \quad \text{Eq. 1}$$

in which DL_e is the detection limit in the equipment (mg L^{-1} or µg L^{-1}), $\bar{X}$ is the average of the element concentration in the blank samples (n = 8), σ is the standard deviation, and t is derived from student t distribution [df = 7 (n - 1); and α = 0.01].

The detection limits (DLs, µg L^{-1}) obtained using GAAS were as follows: As (6.45), Cd (0.81), Pb (12.60), and Ni (3.85). For FAAS, the detection limits (mg L^{-1}) were: Zn (0.06), Cu (0.04), Mn (0.04), and Fe (0.15). The DLs obtained for the soil corresponded to: As (0.13 mg kg^{-1}), Cd (16.2 µg kg^{-1}), Pb (0.25 mg kg^{-1}), Ni (0.08 mg kg^{-1}), Zn (1.20 mg kg^{-1}), Cu (0.90 mg kg^{-1}), Mn (0.70 mg kg^{-1}), and Fe (3.00 mg kg^{-1}). The element recoveries (%) from the 2710A standard were: As (110), Cd (100), Pb (92), Ni (78), Zn (98), Cu (117), Mn (80), and Fe (95).

Water sampling and characterization

As described by Nascimento et al. (2018), PVC tubes (1.5 m long and 0.15 m diameter) were stuck at the upper and middle positions at 1.0-m depths (in wetlands 1, 2, 3, 5, and 6). These tubes functioned as piezometers for water sampling. More protocol details are in Nascimento et al. (2018). Nine sampling points were established per wetland. In the bottom position (Figure 2), water samples were taken from the surface water by immersing a collector pot to a 0.10-m depth. The water sampling occurred monthly from September 2014 to September 2015. After each sample was collected, the pH and electrolytic conductivity (EC) were measured, an aliquot was filtered with a 0.45-µm Millipore® filter, and the elemental composition was measured by inductively coupled plasma optical emission spectrometry (ICP-OES). The pH and EC results were described in Nascimento et al. (2018).

Statistical analysis

Using R software (R Studio Team, 2016), the data was submitted to variance analysis ($p<0.05$) and graphed with error bars. Comparisons between wetlands, layers (0.00-0.20 and 0.40-0.70 m) and sampling positions (P1, upper, middle, and bottom) were made based on standard error bars. Additionally, Pearson correlations between elemental content data and soil properties (clay, CEC, soil organic matter, and pH) were established. Principal component analysis (PCA) was performed for elemental data and soil properties to identify homogenous groups (wetlands and/or sampling positions). The soil trace-element contents were compared to Brazilian threshold values specifically for Minas Gerais State (Copam Normative Deliberation 166/2011). In this work, we use the following terms: background values (quality reference) and threshold values (prevention limit). Both were established by the Copam Normative Deliberation 166/2011. For the discussion, background values obtained for Cerrado soils by Marques et al. (2004) and Campos et al. (2013) were also used.

RESULTS AND DISCUSSION

Principal component analysis of data

Based on the elemental data and soil properties (clay, pH, SOM and its fractions, as well as CEC), the principal Component Analysis (PCA) revealed a clear separation (gradient) of sampling positions (PCA1 - 98.3 %): P1 position (non-hydromorphic region) similar to upper position in the wetlands, followed by middle and bottom positions (Figure 3). This observed gradient was influenced mainly by the soil organic matter content as had also been observed by Ramos et al. (2006), who studied wetland soils in the Triângulo Mineiro region. No differentiations between or groups of wetlands were observed based on the PCA analysis. Cationic elements (mainly Pb^{2+} and Cu^{2+}) were associated with SOM and its fractions, and anionic elements (such as $H_2AsO_4^-$) and Fe were associated with the clay fraction (Figure 3).

Trace-element contents in wetlands soils

The As, Cd, Pb, and Ni contents are shown in figure 4, and the Zn, Cu, Mn, and Fe (not trace) contents are in figure 5. The As content was below the threshold value established by the Brazilian Guidelines (Copam, 2011). In most cases, the As contents for the 0.00-0.20 m layer (Figure 4a) were below of the quality reference value or background content (7.5 mg kg^{-1}) established for the Minas Gerais State, Brazil. A significant increase in the As content at the 0.40-0.70 m layer (Figure 4b) compared to the 0.00-0.20 m layer was observed, mainly for W1 and W5. Since the

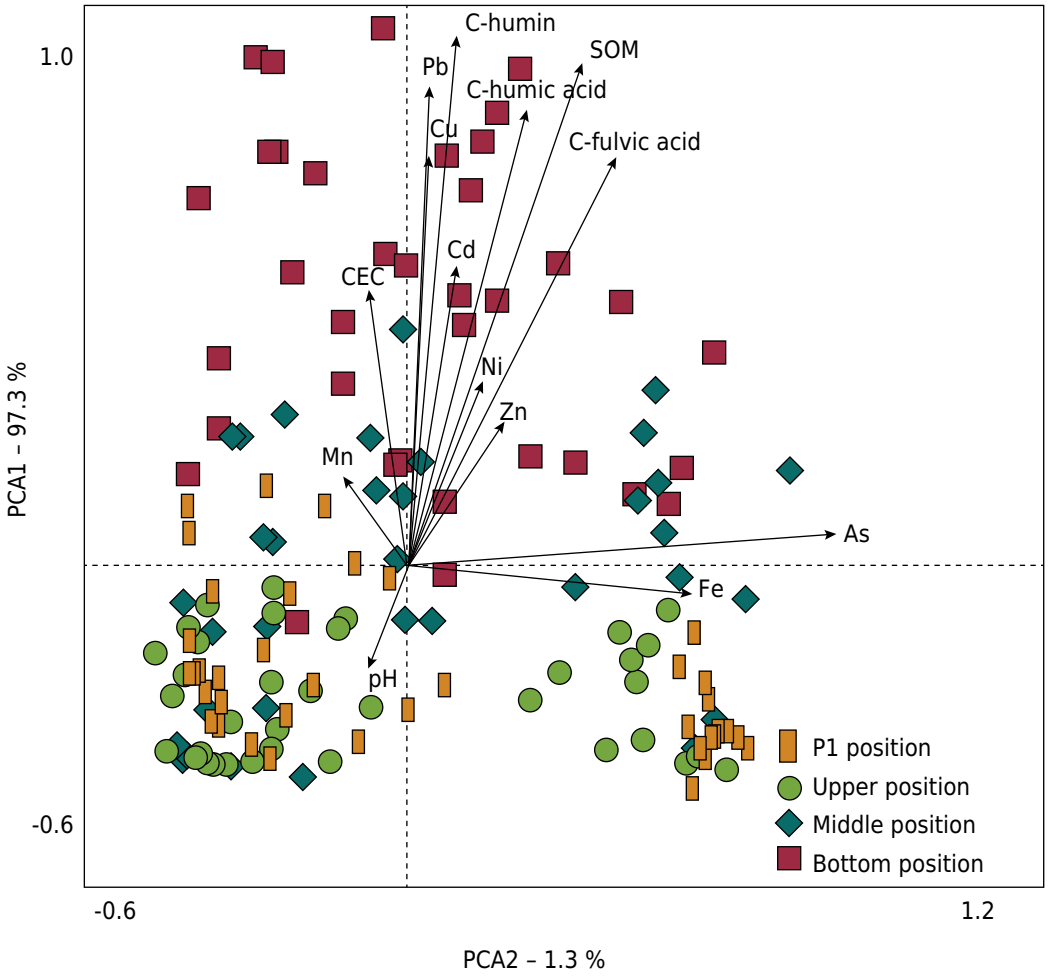

Figure 3. Principal component analysis (PCA) for elemental data distribution and soil properties of the studied wetlands.

0.00-0.20 m layer is richer in organic matter than the 0.40-0.70 m layer (Table 1), this result suggests a negative correlation between the As content and organic matter as has also been suggested by Campos et al. (2013) for non-hydromorphic soils of the Brazilian Cerrado biome. As occurs in soils mainly as $H_2AsO_4^-$ and $HAsO_4^{2-}$, and similar to $H_2PO_4^-$ and HPO_4^{2-}, it has a weak adsorption on negatively charged organic compounds. Thus, the As occurring at the soil surface (organic-rich) may be easily leached to lower layers. In the same region, Rosolen et al. (2015b) also found more As at the subsurface horizons in wetland soils. In soils, As may also occur sorbed on Fe-oxyhydroxides. Thus, as can be seen in figure 6, As contents had a strong correlation with clay content, supporting its possible movement from surface to more clayey subsurface horizons. In wetland soils with hydromorphic conditions, As solubilization and mobility have also been strongly controlled by seasonal Fe dissolution (Davranche et al., 2013). The correlation between As and clay content (Figure 6) may partially explain the higher values found in W1 and W5. These wetlands are typically located in the "Chapada" landform (Ramos et al., 2006) characterized by clayey sediments. The mean clay content for W1 soils at 0.40-0.70 m layer was 802 g kg^{-1}. For W5 (0.40-0.70 m layer) the mean clay content was 643 g kg^{-1}. These high clay contents were not observed for the other wetlands.

The Cd contents (Figures 4c and 4d) were significantly below the background value (400 µg kg^{-1}) and the threshold value (1,300 µg kg^{-1}) (Copam, 2011). The highest Cd content was only 77 µg kg^{-1} in the upper position of the W3 wetland area. In the same region, the average Cd content for non-hydromorphic soils has been previously measured at 1,880 µg kg^{-1} (Campos et al., 2013). In wetland soils affected by different land-uses in China, the Cd content ranged from 790–2,920 µg kg^{-1} (Bai et al., 2010). Zinc was moderately and positively correlated with Cd (Figure 6). In a study of more than 300 wetlands in the USA, the average Cd content was 382 µg kg^{-1} (Jacob et al., 2013), and Cd values were well correlated with Zn and P contents, suggesting the influence of surrounding agricultural activities.

The 0.00-0.20 m layer (Figure 4c) had higher Cd contents than the 0.40-0.70 m layer (Figure 4d). When the superficial layer is richer in organic matter (Table 1), this may contribute to the adsorption of metallic cations like Cd^{2+} (Roth et al., 2012). In both layers, the Cd content increased from the upper position to the bottom position, following the increase in organic matter content. A positive correlation was observed between Cd and SOM fractions (Figure 6). Despite the organic compounds contribution to Cd adsorption, the oxidizing-reducing environment typical of wetlands could affect the mobility and availability of metallic cations (Zhang et al., 2012). In addition, Cd could be associated to dissolved organic matter and have its mobility increased (Ashworth and Alloway, 2008), in association with pH increase under waterlogged conditions.

Additionally, the Pb contents were below the threshold value (72 mg kg^{-1}) (Figures 4e and 4f). Lead contents significantly increased from P1 (non-hydromorphic portion) to the bottom position of wetlands. In the bottom position, the Pb content exceeded the background value (20 mg kg^{-1}). The average Pb content is 9.0 mg kg^{-1} for non-hydromorphic soils developed from sandy sediments in native Cerrado in the Minas Gerais Triangle region (Marques et al., 2004). In other wetland soils of the Cerrado biome region, the Pb content has ranged from 12.1-81.0 mg kg^{-1} (Rosolen et al., 2015a). Lead showed a strong correlation with SOM (Figure 6). Among the SOM fractions, the correlation decreased as follows: C-humin > C-humic > C-fulvic. Lead also showed a strong correlation with Cu.

In general, the Ni contents were below the background value (21.5 mg kg^{-1}) (Figures 4g and 4h). The Ni content exceeded the background value and reached the threshold value only in the W6 wetland area (0.00-0.20 m layer) (Figure 4g). For 0.40-0.70 m layer (Figure 4h), the W6 wetland area also had more Ni than other studied wetlands. Niquel is not directly

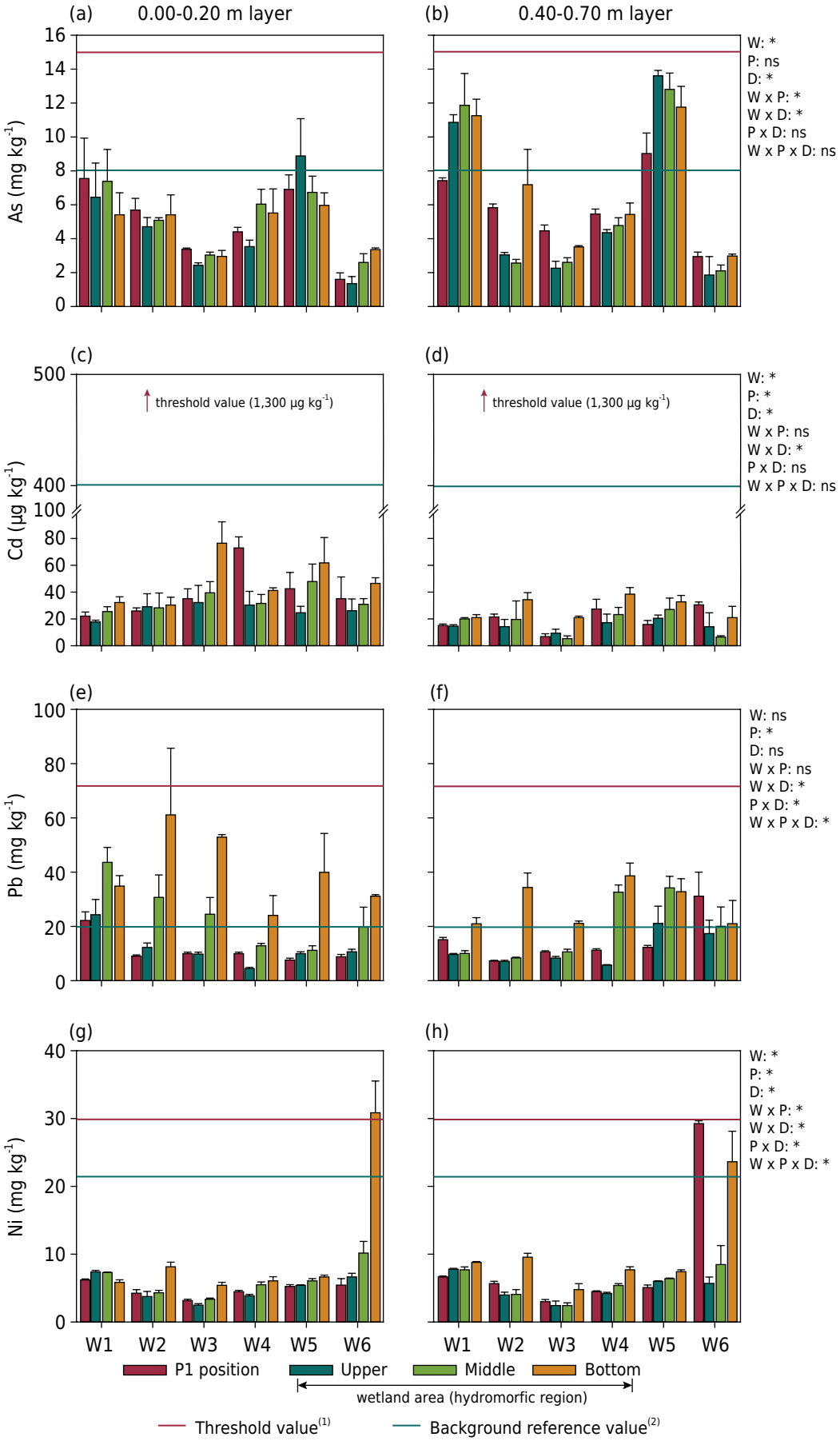

Figure 4. Arsenic, Cd, Pb, and Ni contents in wetland soils of Brazilian Cerrado, Triângulo Mineiro region, Brazil. Error bars indicate the standard error (n = 3). (1) and (2): threshold and background (or quality reference) values established by Brazilian guidelines, Minas Gerais State, Brazil (Copam Normative Deliberation 166/2011).

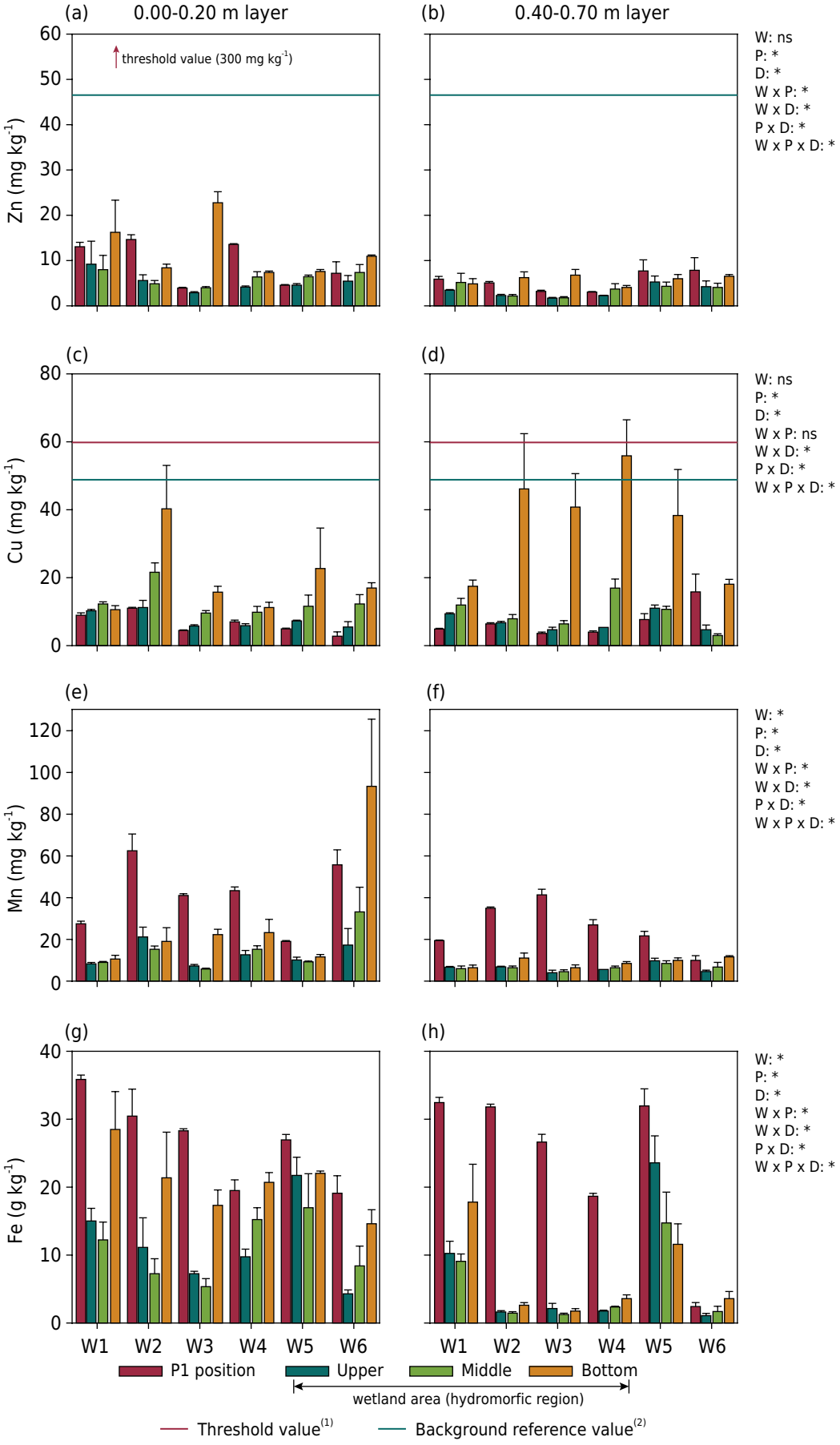

Figure 5. Zinc, Cu, Mn, and Fe contents in wetland soils of Brazilian Cerrado, Triângulo Mineiro region, Brazil. Error bars indicate the standard error (n = 3). (1) and (2): threshold and background (or quality reference) values established by Brazilian guidelines, Minas Gerais State, Brazil (Copam Normative Deliberation 166/2011).

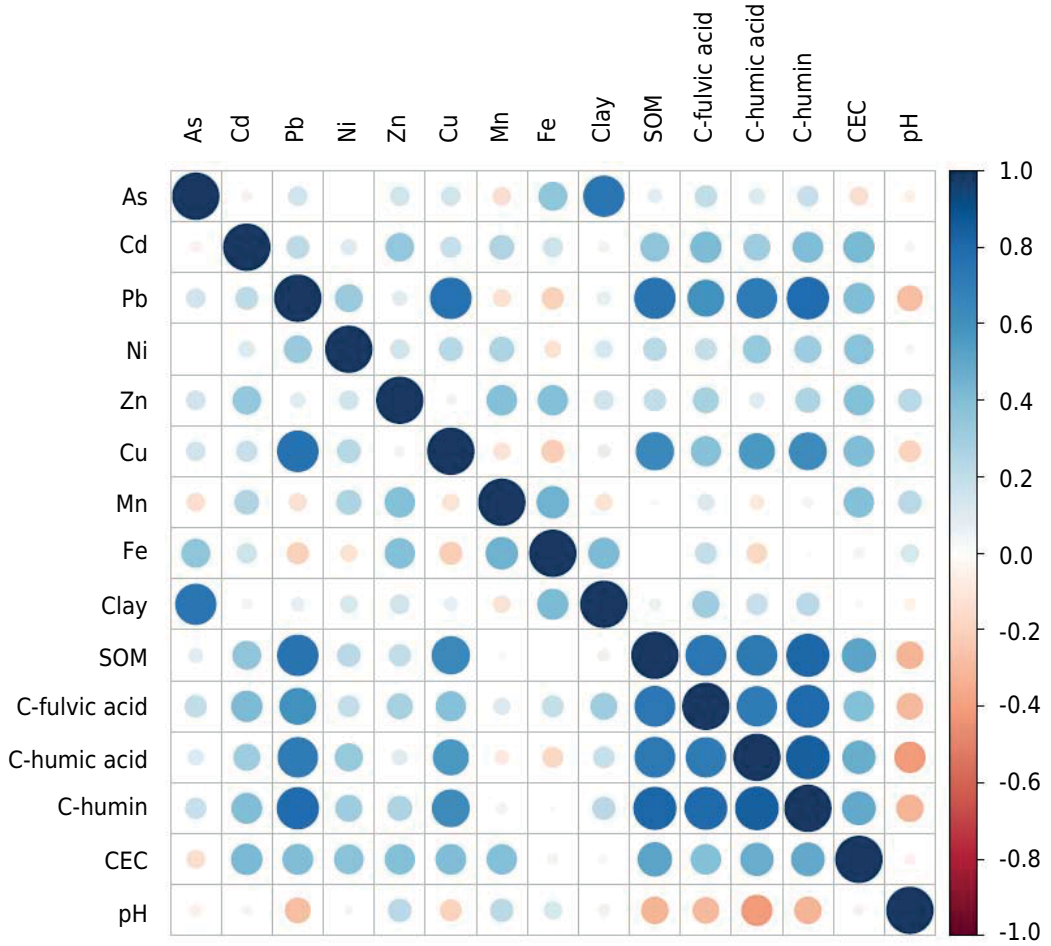

Figure 6. Correlation between As, Cd, Pb, Ni, Zn, Cu, Mn, and Fe contents and some properties of wetland soils from Triângulo Mineiro region, Brazil.

influenced by alternating oxidizing-reducing conditions. Despite its strong adsorption on organic matter, Lockwood et al. (2015) observed that the increase in pH led to the dissolution of organic matter in wetland soils in Hungary and, consequently, increased the Ni availability and mobility. Here, a weak correlation was observed between Ni and SOM fractions (Figure 6). In some wetland soils from France, Grybos et al. (2007) found that Pb and Ni mobility were closely related to Fe reduction and the increase of dissolved organic carbon. These authors concluded that the pH was more important than Eh for the mobility of metallic cations in wetland soils.

Regarding Zn contents (Figures 5a and 5b), the values were well below the background for Cerrado soils. Marques et al. (2004) found the Zn content in well-drained soils from the Cerrado biome ranged from 22-79 mg kg^{-1}. In wetland soils of northwest of Minas Gerais State, Brazil, associated with different land uses, Moraes and Horn (2010) found that the Zn content ranged from 8.9-80.1 mg kg^{-1}. In the Minas Gerais Triangle region, the Zn content in wetland soils was similar to our data, ranging from 5-36 mg kg^{-1} (Marques et al., 2004).

In general, the Cu contents were below 20 mg kg^{-1} for the 0.00-0.20 m layer (Figure 5c). In the wetland soils studied by Rosolen et al. (2015b), the Cu content ranged from 31-88 mg kg^{-1}. These authors emphasized that the main contamination risk of Cerrado's wetlands is from Cu, As, and Cr. In Poyang Lake (China), the Cu contents in wetland soils ranged from 6.83-342.54 mg kg^{-1} and were mainly sorbed on the organic residual fraction (Wang et al., 2017). For some wetland areas (W2, W3, W4, and W5), a significant increase in Cu content was observed at the bottom position (0.40-0.70 m layer)

(Figure 5d) compared to the 0.00-0.20 m layer (Figure 5c). Despite the tendency of Cu to be highly adsorbed on organic matter and compounds, its solubility and mobility are controlled by pH and dissolved organic matter (Lockwood et al., 2015). These authors suggested that humic acid dissolution in both aerobic and anaerobic conditions might increase the Cu mobility.

In Minas Gerais State, Brazil, there are not yet background and threshold values established by the Environmental Foundation (Copam Normative Deliberation 166/2011) for Mn. The highest Mn content found here was 96.5 mg kg^{-1} at the bottom position of W6 wetland area (0.00-0.20 m layer) (Figure 5e). For the 0.00-0.20 m layer, the average Mn contents at the P1, upper, middle, and bottom positions were: 41.7, 13.1, 14.9, and 30.3 mg kg^{-1}, respectively. At the 0.40-0.70 m layer (Figure 5f), the Mn contents were lower: 26.0, 6.6, 6.8, and 9.4 mg kg^{-1}. For both layers, the Mn content was higher at the P1 position (well-drained environment) compared to the hydromorphic portions of wetlands. In an anaerobic environment, Mn^{4+} is reduced to Mn^{2+} and easily leached from the soil. For the soils studied, even when considering land use effects, the Mn contents were lower than the free-drained soils of the Cerrado biome (216 mg kg^{-1}) (Marques et al., 2004).

The occurrence of Fe (not as a trace element) in waterlogged soils is important due to oxidation-reduction reactions, which control the availability and mobility of other elements. The Fe contents ranged from 11.74 g kg^{-1} (at the upper position) to 20.75 g kg^{-1} (at the bottom position) at the 0.00-0.20 m layer (figure 5g). For the 0.40-0.70 m layer (Figure 5h), the content ranged from 6.76-6.84 g kg^{-1}. As expected, samples from the non-hydromorphic portion (P1) dominated by *Latossolos Vermelhos* had significantly higher Fe contents than upper, middle, and bottom positions in the wetland soils. In hydromorphic conditions, the Fe^{3+}, as the final acceptor of electrons, is reduced to Fe^{2+} with redox potential values between 100-300 mV. In a waterlogged experiment under laboratory conditions, it was observed that the soil samples from the same wetlands we studied here had a redox potentials between 100-300 mV after 16 days of flooding (Nascimento et al., 2018). The Fe^{2+} is mobile and can be translocated to the soil profile at greater depths and/or leached by water (Camargo et al., 1999). For this reason, in wetlands occur Gleysols seasonally flooded (Ramos et al., 2006). In reduction conditions, Grybos et al. (2007) found an increase in Fe^{2+} content and dissolved organic carbon in wetland soils. In turn, Davranche et al. (2013) found that dissolved organic matter influences Fe mobility, due to the possible interaction between Fe^{2+} and organic matter. A significant increase of Fe content from the upper/middle to the bottom position can be seen in figure 5g (0.00-0.20 m layer). However, a correlation between Fe and SOM was not observed. Iron positively was correlated with Zn, Mn, and clay content (Figure 6). The increase of Fe at the bottom position may be related to green rust formation along the soil-water interface at the bottoms of wetlands. Green rusts are Fe(II)-Fe(III) hydroxyl salts in weakly reducing acid environments. Due to their high reactivity, the green rusts are well known for adsorbing pollutants in wetland soils (Chaves, 2005).

Except for Fe and Mn, all cationic elements positively correlated to SOM and its fractions (Figure 6). The correlation with SOM decreased as follows: Pb > Cu > Cd > Ni > Zn. Except for Ni, this trend corroborates the higher interaction of Pb and Cu with SOM compared to Cd and Zn. In addition, the correlation with SOM fractions was higher for C-humin acid, followed by C-humic and C-fulvic acids. The lack of correlation between SOM and Fe or Mn may be due to the fact these elements are subjected to reduction reactions in hydromorphic conditions, and can be easily released as Fe^{2+} and Mn^{2+}.

In our results, there was no increase observed of trace-element contents in the disturbed wetland soils (W1, W2, W4, and W6) compared to undisturbed wetland soils (W3 and W5). In all wetlands, in most of cases (82 %), the trace-element contents were below the

Table 2. Elemental composition obtained by ICP-OES of water from Cerrado wetlands, Uberlândia region, Minas Gerais State, from September 2014 to September 2015

W	Position	Value	n	Al	Ca	Fe	K	Mg	Mn	P	S	Si	Zn
				mg L^{-1}									
	Upper	Avg.	30	<LD	0.66	0.33	1.23	0.14	<LD	0.05	0.03	0.73	<LD
	Upper	Min.		<LD	0.21	0.14	0.93	0.10	<LD	0.02	<LD	0.07	<LD
	Upper	Max.		<LD	2.57	1.25	2.45	0.29	0.01	0.15	0.14	1.27	0.01
	Middle	Avg.	34	0.09	0.82	1.23	1.24	0.17	<LD	0.04	0.02	0.80	0.01
1	Middle	Min.		<LD	0.20	0.21	0.96	0.09	<LD	0.02	<LD	<LD	<LD
	Middle	Max.		1.99	3.04	4.41	2.20	0.37	0.01	0.10	0.20	1.51	0.41
	Bottom	Avg.	34	0.10	0.34	0.31	1.16	0.10	<LD	0.04	0.02	1.05	<LD
	Bottom	Min.		<LD	0.03	0.14	0.90	0.07	<LD	0.02	<LD	0.29	<LD
	Bottom	Max.		3.19	2.38	2.20	1.59	0.19	0.01	0.13	0.10	1.90	0.06
	Upper	Avg.	3	<LD	0.36	0.20	1.35	0.21	0.01	0.04	0.02	1.18	<LD
	Upper	Min.		<LD	0.28	0.17	1.27	0.19	0.01	0.03	<LD	0.86	<LD
	Upper	Max.		0.01	0.46	0.24	1.42	0.22	0.02	0.05	0.03	1.62	<LD
	Middle	Avg.	5	0.03	0.42	0.26	1.34	0.17	0.01	0.04	0.03	0.90	<LD
2	Middle	Min.		<LD	0.16	0.15	1.07	0.08	<LD	0.02	<LD	0.71	<LD
	Middle	Max.		0.14	0.70	0.41	1.58	0.27	0.01	0.05	0.10	1.12	<LD
	Bottom	Avg.	37	0.04	0.34	0.32	1.12	0.18	0.01	0.04	0.02	3.72	<LD
	Bottom	Min.		<LD	0.12	0.14	0.89	0.10	<LD	0.02	<LD	2.02	<LD
	Bottom	Max.		1.43	1.34	1.28	1.66	0.31	0.18	0.13	0.11	5.17	<LD
	Upper	Avg.	9	0.10	1.08	0.37	1.16	0.10	0.01	0.04	0.07	0.98	<LD
	Upper	Min.		<LD	0.50	0.16	1.07	0.08	0.08	0.02	<LD	0.60	<LD
	Upper	Max.		0.85	2.44	0.71	1.42	0.15	0.01	0.05	0.21	1.55	<LD
	Middle	Avg.	25	0.35	0.71	0.24	1.17	0.13	0.01	0.04	0.06	1.80	<LD
3	Middle	Min.		<LD	0.50	0.16	1.07	0.08	<LD	0.02	<LD	0.60	<LD
	Middle	Max.		8.58	11.96	0.41	1.60	0.37	0.01	0.13	0.14	2.94	0.01
	Bottom	Avg.	35	0.05	0.28	0.25	1.08	0.10	<LD	0.04	0.03	1.91	0.01
	Bottom	Min.		<LD	0.06	0.13	0.89	0.07	<LD	0.02	<LD	0.55	<LD
	Bottom	Max.		0.80	1.72	0.90	1.43	0.20	0.01	0.18	0.20	3.07	0.40
	Upper	Avg.	13	0.04	0.72	0.32	1.17	0.12	0.01	0.04	0.06	1.67	<LD
	Upper	Min.		<LD	0.16	0.16	0.92	0.08	0.01	0.02	<LD	0.72	<LD
	Upper	Max.		0.29	3.37	1.07	1.42	0.17	0.01	0.05	0.30	2.85	<LD
	Middle	Avg.	32	0.21	1.42	0.35	1.17	0.13	0.01	0.04	0.07	1.91	<LD
5	Middle	Min.		<LD	0.10	0.14	0.92	0.08	<LD	0.02	<LD	1.25	<LD
	Middle	Max.		4.79	6.11	1.33	1.54	0.26	0.02	0.13	0.30	2.70	<LD
	Bottom	Avg.	34	0.04	0.26	0.34	1.07	0.10	<LD	0.05	0.02	2.08	<LD
	Bottom	Min.		<LD	0.04	0.14	0.93	0.07	<LD	0.02	<LD	1.05	<LD
	Bottom	Max.		0.72	1.05	1.06	1.37	0.14	0.01	0.18	0.10	3.47	<LD
	Upper	Avg.	14	0.83	1.02	0.25	1.20	0.19	0.01	0.04	0.02	2.05	<LD
	Upper	Min.		<LD	0.23	0.14	0.94	0.09	<LD	0.03	<LD	1.07	<LD
	Upper	Max.		6.76	4.26	0.39	1.64	0.56	0.04	0.06	0.07	2.97	<LD
	Middle	Avg.	21	0.44	1.02	0.51	1.29	0.29	0.02	0.04	0.03	3.38	<LD
6	Middle	Min.		<LD	0.30	0.17	1.00	0.13	<LD	0.02	<LD	2.37	<LD
	Middle	Max.		3.24	4.26	3.02	2.05	0.85	0.12	0.10	0.12	4.61	<LD
	Bottom	Avg.	25	0.03	2.46	0.88	1.39	0.89	0.02	0.04	0.04	4.94	<LD
	Bottom	Min.		<LD	0.24	0.15	1.06	0.12	<LD	0.02	<LD	3.22	<LD
	Bottom	Max.		0.85	7.25	6.14	3.58	2.40	0.07	0.22	0.13	7.15	<LD
		Σn	351	-	-	-	-	-	-	-	-	-	-
		Avg.	-	0.16	0.85	0.45	1.18	0.20	0.01	0.04	0.03	2.06	0.00

W = wetland; Avg = average; Min = minimum value found; Max = maximum value found; n = number of collected water samples in each wetland and sampling position from September 2014 to September 2015; LD = detection limit (mg L^{-1}): Al = 0.023; Ca = 0.056; Cu = 0.009; Fe = 0.113; K = 0.005; Mg = 0.019; Mn = 0.007; P = 0.019; S = 0.028; Si = 0.021; Zn = 0.009. Quantification of elements via ICP-OES after filtration (0.45 µm Millipore® filter).

background contents established by the Brazilian guidelines for non-hydromorphic soils. The difference between disturbed and undisturbed wetland soils could be attributable to inherent spatial variations in trace-element contents in soils as affected by geological features. Our results can serve as a reference for Cerrado wetland soils in further contamination investigations.

Elemental characterization of water from wetlands

The following elements were detected and quantified in the water samples (Table 2): Al, Ca, Fe, K, Mg, Mn, P, S, Si, and Zn. Potential environmental pollutants like As, Cd, Cu, Pb, and Ni were below the detection limits of ICP-OES. Significant differences between wetlands and sampling positions (Table 2) were not observed, and the concentrations obtained for all elements were quite low, especially for Al, Mn, S, and Zn. According to the Environmental National Council (Conama Resolution 357/2005), water bodies classified as Type I can contain up to the following concentrations (mg L^{-1}): Al (0.10), Fe (0.30), P (0.02), Mn (0.10), and S (250). For water bodies Type III: Al (0.20); Fe (5.00); P (0.05); Mn (0.50); S (250). The Conama Resolution 357/2005 does not establish guidelines for K, Ca, Mg, and Si. For Al, the global average has been determined to be 0.16 mg L^{-1}. In most of cases (66 %), Al concentration was less than or equal to 0.1 mg L^{-1}, and the maximum value found was 8.58 mg L^{-1}. For Fe, the global average was found to be 0.45 mg L^{-1}, and for each wetland and sampling position, the concentration was less than 0.50 mg L^{-1}. In general, the P concentration was 0.04 mg L^{-1}. For Type I and III water bodies, the Conama Resolution 357/2005 establishes 0.02 and 0.05 mg L^{-1} as maximum values, respectively. For sub-superficial water, the Environmental Foundation of Minas Gerais State (Copam Normative Deliberation 166/2011) establishes the following maximum concentration values (mg L^{-1}): Al (3.50), Cu (2.00), Fe (2.45), Mn (0.40), and Zn (1.05). Ramos et al. (2006) evaluated the elemental composition of water from wetlands in the Triângulo Mineiro Region. These authors quantified the concentrations of Ca (0-2.73 mg L^{-1}), Mg (0.01-1.41 mg L^{-1}), Fe (0.7-1.3 mg L^{-1}), Cl (0.08-1.33 mg L^{-1}), Cu, Zn, and Mn (0-0.03 mg L^{-1}). The elemental concentrations of water from the Arenito Bauru landform (sandier) tends to be higher than those of the “Chapada” surface (more clayey), suggesting a higher potential of contamination of wetland soils surrounded by sandy sediments.

CONCLUSIONS

In the six wetland areas surrounded by representative livestock-crop-forestry production in the Cerrado biome, the As, Cd, Pb, Ni, Zn, Cu, Mn, and Fe contents in the wetland soils were below the threshold values established by Brazilian guidelines, mainly for Cd. The distribution of soil trace elements (cations and oxi-anions) was well correlated with soil organic matter and its fractions. The elemental concentrations (Al, Ca, Fe, K, Mg, Mn, P, S, Si, and Zn) in water from the wetlands studied were quite low. These data improve the poor inventory of Cerrado wetland soils of Brazil, regarding the baseline elemental contents, and constitute an important reference for further studies.

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