USE OF LEGAL RESERVE AREAS AS GEOCHEMICAL BACKGROUND IN HYDROSEDIMENTOLOGY STUDIES(1)

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SUMMARY

In hydrosedimentology studies the determination of the trace element concentrations at the study site is imperative, since this background can be used to assess the enrichment of sediments with these elements. This enrichment can be the result of the natural process of geological formation or of anthropogenic activities. In the latter case, guidelines are used to indicate the concentrations at which trace elements cause ecotoxicity effects on the environment. Thus, this study used legal reserve areas in the municipality of Toledo, PR, where natural forests are maintained, with no or minimal human interference to establish background levels. The results of atomic emission spectrometry with inductively coupled argon plasma showed that the legal reserves have lower levels of trace elements than other theoretical references, but equivalent concentrations to the safety levels recommended by international guidelines. It was concluded that determining values is fundamental to recommend this background as scientific database for research in the area of hydrosedimentology of this site and also as a way of environmental management of the watershed of this municipality.

Index terms: natural heavy metal levels, conservation areas, environmental quality.

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RESUMO: *UTILIZAÇÃO DE ÁREAS DE RESERVA LEGAL COMO* BACKGROUND *GEOQUÍMICO EM ESTUDOS HIDROSSEDIMENTOLÓGICOS*

Em estudos de hidrossedimentologia é imprescindível que se tenha o levantamento dos teores de elementos-traço do local de pesquisa, uma vez que esse background pode ser utilizado para interpretações do enriquecimento desses elementos no local da pesquisa. Esse enriquecimento pode estar relacionado ao processo natural de sua formação geológica ou às ações antropogênicas, sendo nesse último caso utilizado os guidelines, *que apresentam as concentrações em que os elementos-traço causam efeitos de ecotoxicidade no ambiente. Assim, este estudo utilizou áreas com florestas naturais denominadas de reserva legal para formação do* background *do município de Toledo, PR, as quais asseguram condições de nenhuma ou mínima interferência antrópica. Os resultados da espectrometria de emissão atômica com plasma de argônio acoplado indutivamente demonstraram que as reservas legais possuem teores de elementos-traço inferiores aos demais referenciais teóricos pesquisados, porém em concentrações equivalentes aos níveis de segurança dos recomendados pelos* guidelines *internacionais consultados. Concluiu-se que os valores determinados são fundamentais para recomendar esse* background *como base de dados científicos para pesquisas da área de hidrossedimentologia desse local e também como forma de gerenciamento ambiental da bacia hidrográfica desse município.*

Termos de indexação: teores naturais de metal pesado, áreas de preservação, qualidade ambiental.

INTRODUCTION

Human activities may directly and significantly contribute to environmental contamination by trace elements (TEs), whereas high concentrations in the soil may interfere with the environment, changing the productivity, biodiversity and sustainability of ecosystems as well as posing risks to humans and animals (Kede et al., 2008). The potential damage by these elements is aggravated when absorbed by plants and when exceeding the maximum retention capacity of the soil, becoming easily leachable, resulting in groundwater discharge (Pandolfo et al., 2008).

In Brazil, a set of guiding values for environmental soil quality is defined by Resolution Nº 420/2009 of the National Environmental Council (Conama) and by a Normative Rule Nº 195/2005-E of the Environmental Protection Agency in São Paulo (Cetesb), establishing Reference Quality Values (RQV), Prevention Values (PV) and Investigation Values (IV). Thus, the RQV for each of the TEs is based on the analysis of soil under natural conditions (without or with minimal human interference), while PV and IV are determined by assessing and analyzing the environmental risk (Conama, 2009).

According to Galuszka (2007), one of the most important issues in recent environmental studies concerns the establishment of geochemical background values for organic elements and compounds in biotic and abiotic systems. According to the author, the relationship between natural changes and those caused by anthropogenic action on chemical species is an issue with important implications in the fields of geology, biology and toxicology and other fields of knowledge. This is particularly important when a geochemical analysis of toxic element concentrations is required.

Thus, *background* is defined as a theoretically natural concentration of a substance or element in a sample, considering the temporal and spatial variables in the area under investigation (Galuszka, 2006). Also, the *International Organization for Standardization* (ISO, 2005) recommends that the environmental background of a substance or metal in the soil be defined as a frequency distribution parameter of commonly found levels, i.e., the natural contents of these elements in the soil (Zhao et al., 2007).

Given the lack of specific regional backgrounds that can support studies on hydrosedimentology, this paper establishes a background for eutroferric Red Latosol with the use of soil samples with preserved/undisturbed characteristics of the geological formation, and, consequently, unaltered levels of trace elements, for being located in legal reserves of rural properties in Toledo, PR.

MATERIAL AND METHODS

Figure 1a,b shows Toledo in western Paraná, and the five legal reserves in the surroundings of the municipality (Table 1).

The soil is classified as eutroferric Red Latosol with a low silt/clay ratio and the absolute or virtual absence of easily weatherable primary minerals (Embrapa, 2013). In each of the five legal reserves, soil samples were randomly extracted with a stainless steel shovel from a depth of 0-20 cm. One of the three samplings was carried out in the rainy season to eliminate any hydrodynamic influence on TE concentrations.

In the laboratory, samples were dried in an air circulation oven at 45 °C and after cooling, ground in

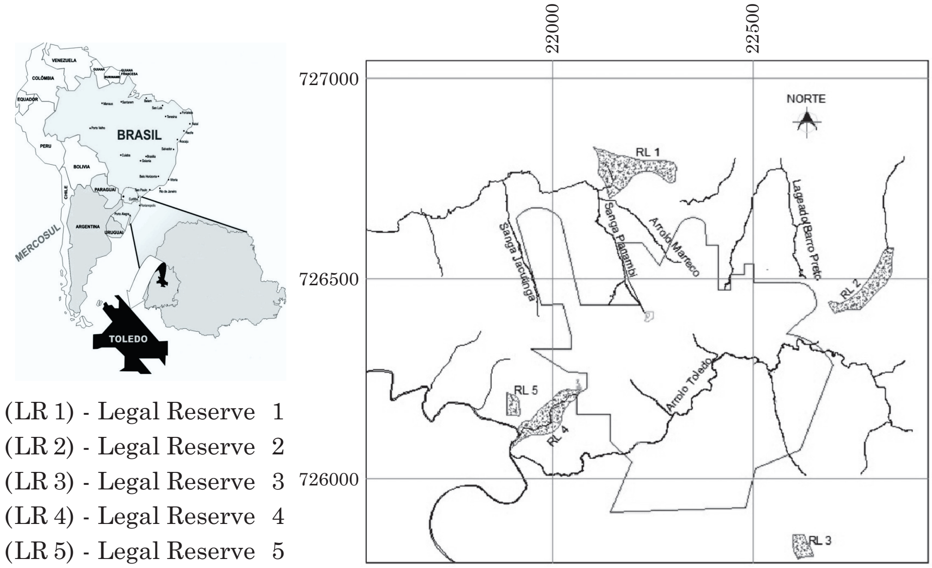

Figure 1. Geographical location of the study area (a) South America, Brazil, Paraná, Toledo; and (b) urban perimeter and location of legal reserves.

Table 1. Sampling description (geochemical background) in study areas

Point	Geographic coordinate	Location	Legal reserve characteristic	Altitude m
LR1	S 24° 40' 48" - W 53° 45' 21"	Northern region	Vegetation of subtropical broadleaf forest, with predominant species of peroba tree (*Anpidosperma polyneuron*), cedar (*Cedrela odorata*), cabreúva (*Myroxylon perniferun*), bay laurel (*Laurus nobilis*), pau-d'alho *(Gallesia integrifolia)*, ipê (*Tabebuia* spp.), pau marfim (*Balfourodendron riedelianum)* and others	585
				578
LR2	S 24° 42' 35" - W 53° 41' 23"	Northeast region		580
LR3	S 24° 46' 10" - W 53° 42' 16"	Southern region		492
LR4	S 24° 44' 49" - W 53° 45' 59"	Southwest region		
LR5	S 24° 43' 59" - W 53° 46' 10"	East region		571

an agate mortar and sieved (<2 mm) through Teflon mesh to recover approximately 10 g of the soil fraction (Conama, 2009). To digest the samples, the updated USEPA 3051 method was used (microwave) of the *American Public Health Association* (APHA, 1998), as recommended by Conama n^o 420/2009. The analytical practice of the *Standard Methods* (22nd 2011) method by inductively coupled plasma-atomic emission spectroscopy (ICP-OES), model Optima 8000 ICP - Perkin Elmer.

The data were transformed by the logarithm function: log (x +1), as the results had a large variation in dimensional values resulting in a positive asymmetrical distribution. To determine the background, the descriptive and multivariate statistical analysis was chosen, and in the latter case, data were reoriented by Principal Component Analysis (PCA), in which the axes were selected based on the "Broken Stick" (Jackson, 1993) randomization model.

RESULTS AND DISCUSSION

Table 2 shows efficiency parameters of the applied analytical methods, by comparison of the concentrations of the species of interest with the standard reference material Green River Shale, SGR-1b from USGS (United States Geological Survey).

The mean results and their relative deviations (extraction efficiency) from the reference standard were obtained in aqueous matrices with minimum limits of quantification. The chemical analysis included concentration ranges significantly close to those expected. The accuracy calculated by the relative standard deviations (RSD) varied from 3.66 to 9.63 % for Cu and Pb, respectively; and, therefore, less than 10 % for all elements analyzed. According to Milagres et al. (2007), for accurate and reproducible results, the coefficient of variation (CV) in a series of determinations (precision) can vary up to 10 %, while the CV between different series (reproducibility) should be less than 20 %. Considering that the 3051A method using concentrated nitric acid is a method of incomplete sample decomposition, the recovery rates in this study were very significant for all elements analyzed compared with other studies with much more energetic digestions, as used by Vieira et al. (2005).

Regional reference values (RRV)

Table 3 shows the results of a descriptive statistical analysis to determine the local background levels referred to in this study as the regional reference values (RRV).

As reported by Ker (1997), the eutroferric Red Latosols collected in legal reserves are clayey or very clayey, a texture condition given by the low quartz concentration in the source material. The same author stated that the mineralogy of this type of Latosol typically has a coarse fraction of magnetite (FeO, Fe_2O_3) with predominance of magnetite intergrown with ilmenite ($FeTiO_2$), resulting in the high Fe concentrations (105,956 mg kg^{-1}) observed in this study. The significant concentrations of other TEs also indicate the potential fertility of this soil due to the presence of total P and some trace elements, such as Mn, Ni, Cu, Zn, and Co (Ker, 1997).

The results in table 3 show concentrations below 0.005 (As and Se), 0.01 (U) and 0.1 (B) in mg kg^{-1}, indicating little potential for dispersion of these elements in this watershed. It was expected that the B contained in the soil organic fraction of these legal reserve would range from 0.1 to 0.6 mg kg^{-1}, but according to Rosolem & Bíscaro (2007), this element can be largely reduced by leaching losses.

Table 2. Values obtained from the *Green River Shale* reference sample (SGR-1b) of USGS

Element	Blank	Standard		Determined by ICP - OES	
		Mean ± SD	RSD	Mean ± SD	RSD
As	< 0.005	67 ± 5	7.46	34.52 ± 2.87	8.32
Ba	0.003	290 ± 40	13.79	221.22 ± 15.66	7.08
Cu	0.013	66 ± 9	13.63	64.15 ± 2.34	3.66
Cd	0.008	0.9	-	0.79 ± 0.07	8.86
Cr	0.016	30 ± 3	10.00	26.26 ± 1.01	3.85
Mn	0.003	267 ± 34	12.73	209.88 ± 9.53	4.54
Ni	0.005	29	-	21.63 ± 1.38	6.74
Pb	0.017	38 ± 4	10.52	33.72 ± 3.25	9.63
Zn	0.048	74 ± 9	12.16	61.75 ± 5.27	8.54

SD: standard deviation; RSD: relative standard deviations.

Table 3. Mean regional reference values (RRV) obtained from the five legal reserves

Metal	n(1)	$\bar{x}$ (RRV)(2)	σ(3)	CV(4)	CI(5) (α = 95 %)
				%	
Al	15	102,372	551	0.54	101,828 - 103,599
As	10	< 0.005	-	-	-
B	10	< 0.1	-	-	-
Ba	15	62.51	28.56	45.69	32.86 - 128.89
Cu	15	212.3	57.20	26.95	114.40 - 322.60
Cd	10	0.69	0.10	13.83	0.55 - 0.90
Cr	15	54.2	19.63	36.22	16.02 - 92.78
Fe	15	105,956	666	0.63	104,699 - 107,141
Mn	15	916.4	342.1	37.33	537.7 - 1,707.7
Mg	15	2,303.2	136.1	5.91	2,036.2 - 2,440.3
Na	15	1493.1	346.2	23.19	1,009.1 - 2,367.9
Ni	15	30.26	9.55	31.56	8.62 - 43.94
Pb	15	17.46	2.39	13.68	12.57 - 20.69
Sb	15	4.58	0.69	15.10	3 - 5.87
Se	10	< 0.005	-	-	-
U	10	< 0.01	-	-	-
Zn	15	82.14	13.79	16.79	57.91 - 114.97

(1) n: number of repetitions; (2) $\bar{x}$: mean (RRV: Regional Reference Values); (3) σ: standard deviation; (4) CV: coefficient of variation; (5) CI: confidence interval.

The analysis of the coefficients of variation may indicated great variability in the concentrations of RRV, although the concentrations were, on average, higher than the quality reference values proposed for metals in soils of São Paulo by Casarini (2000) for the elements: Cd (0.5), Cu (35.1), Cr (40.2), Ni (13.2), Pb (17), and Zn (59.9) in mg kg^{-1} and were also higher than those proposed by Campos et al. (2003) for 19 Brazilian Latosols, using the same method (USEPA 3051A) for the elements: Cd (0.66 ± 0.19), Cu (65 ± 7.4), Ni (18 ± 12), and Zn (39 ± 24) in mg kg^{-1}. Thus, different land uses could explain the lower values obtained in this study and, on the other hand, demonstrate that legal reserves maintain higher levels of these elements for preserving their original characteristics of their formation.

The current understanding of the soil quality concept is based on the balance between geological, hydrological, chemical, physical, and biological soil conditions (Sposito & Zabel, 2003), but metals such as Al, Fe and Mn, presenting RRV in high average concentrations of 102,372, 105,956 and 916.4 mg kg^{-1}, respectively, may interfere with the concentration of other metals, since their oxides and hydroxides are minerals that occur in discrete phases or in combination with other minerals in the form of coatings, aside from having a high specific surface, micropores and different adsorption sites, which gives them a significant action in mobility, distribution and attenuation of trace metals (Axe & Trivedi, 2002). Also, the metals Pb, Cu, Zn and Ni, despite not changing their oxidation state, may be indirectly affected by changes in the soil redox potential for their strong association with Fe and Mn oxides, which are susceptible to changes in the oxidation state (Axe & Trivedi, 2002). In expansive clay minerals and the oxides and hydroxides of Fe, Al and Mn, metals can also be trapped in negative sites present in the crystal structures (octahedral spaces), forming inner sphere complexes (Sposito, 2008).

Table 4 shows the Pearson correlation analysis ($p<0.05$), eigenvalues, percentage of explanation and the “Broken-Stick” value. Problems occurred in the digestion of the samples and the variables with zero values were presented together with indices 1 or 2, for the lowest and highest number of repetitions, respectively.

This correlation table was organized in decreasing order, with the largest negative or positive factorial loads indicating extreme TE concentrations in this mineralogical matrix, since correlations can identify and quantify variations in soil associated with pedogenic processes (Carvalho Junior et al., 2008). High positive correlations (> 0.8) mainly for Mn_2 and Fe_2; and negative correlations (< -0.8) for the elements Ni_2, Cr_2, Sb_2 and Pb_2 are not always of environmental interest. For example, Mn oxides can be bound to essential TEs for plants (Co, Cu, Zn, or Mo) and also strongly adsorb polluting elements such as Pb and Cd, which, at higher concentrations, had toxic effects on eutroferric Red Latosols in the region of Missões, Rio Grande do Sul (Meurer, 2006).

Through eigenvalues greater than expected at random, the principal component analysis (PCA) summarized the three main components according to the Broken-Stick criteria. Thus, figure 2 shows the graphs of the first three principal components (PC), to observe the behavior of variables included in each of these components as well as the variable behavior in the legal reserves (LR).

The first component (PC1), with an eigenvalue of $\lambda=9.91$ (Table 4), accounted for 52 % of the variability and was influenced by most metals, more positively by Mn, Fe, Ba, and Al and negatively by Na, Zn, Ni, Mg, Cr, Sb, and Pb, with high bivariate correlations ($r > 0.60$). This component segregated LR5 (Figure 2) from the others by presenting, together, the highest concentrations of metals with positive association and the lowest concentrations of metals with negative association.

The second component (PC2), with an eigenvalue of $\lambda=5.58$, accounted for 29 % of the variability and was influenced by only five metals - positively by Ba, Mn, Cu, Cr, and Ni and with high bivariate correlations ($r > 0.6$); and negatively by none of the metals. This component segregated LR4 from the others by the concentration of metals with positive association for this set of elements (Figure 2). Finally, the third component (CP3) showed an eigenvalue of $\lambda=2.84$ and accounted for only 15 % of the variability, and was negatively influenced by the metals Zn1, Cd1 and Na2 with high bivariate correlations; this component segregated LR1 (Figure 2) from the others by concentrations of other metals with negative association for this set of elements.

The results show that the most complete analysis (n=15) defines the ordering of the variables with indices 2 in CP1, and thus explain most of the information in the original data set which makes the visualization more direct and, therefore, the subsequent analyses more practical (Lattin et al., 2011). Figure 2 shows that CP1 is highely similar to LR2 and LR5, which are located on opposite sides of the municipality. The LR4 is located near LR5 and is ordered in different components and LR1 kept its ordination in both projections and is located north of the city. Thus, these results and observations show that the legal reserves are apparently homogeneous due to their formation and preservation characteristics, but this homogeneity cannot be applied to TEs, due to the geochemical differentiation of the earth’s crust, which affects the differential distribution of TEs within the same geological formation (Mello & Abrahão, 2013).

The three components explained 96 % of the variability and no source of geogenic or anthropogenic

Table 4. Values of correlation, eigenvalues, percentage of explanation and "Broken Stick" retention coefficient for variables of legal reserves

	CP1	CP2	CP3	Mn2	Fe2	Al2	Ba2	Ba1	Mn1	Cr1	Cu1	Ni1	Zn1	Cd1	Na2	Cu2	Zn2	Ni2	Mg2	Cr2	Sb2	Pb2
Mn2	**0.9**	0.0	-0.3	**1.0**																		
Fe2	**0.9**	0.3	-0.4	**0.8**	**1.0**																	
Al2	**0.7**	0.6	-0.1	**0.5**	**0.9**	**1.0**																
Ba2	**0.7**	0.6	-0.3	**0.8**	**0.8**	**0.7**	**1.0**															
Ba1	-0.1	**1.0**	-0.2	0.0	0.2	0.5	**0.5**	**1.0**														
Mn1	-0.2	**0.9**	-0.4	-0.1	0.3	**0.5**	0.4	**0.9**	**1.0**													
Cr1	0.4	**0.9**	0.3	0.3	0.4	**0.7**	**0.7**	**0.7**	**0.5**	**1.0**												
Cu1	0.6	**0.8**	0.3	0.4	**0.6**	**0.8**	**0.7**	**0.6**	0.5	**1,0**	**1.0**											
Ni1	0.6	**0.7**	0.2	0.4	**0.7**	**0.9**	**0.7**	**0.6**	0.5	**0.9**	**1.0**	**1.0**										
Zn1	0.3	0.1	**-1.0**	**0.6**	**0.6**	0.3	**0.6**	0.3	0.4	-0.1	0.0	0.0	**1.0**									
Cd1	-0.6	0.0	**-0.8**	-0.3	-0.2	-0.3	-0.2	0.3	0.4	-0.5	**-0.6**	**-0.6**	**0.6**	**1.0**								
Na2	**-0.6**	-0.5	**-0.6**	-0.4	-0.4	**-0.6**	**-0.5**	-0.2	0.0	**-0.8**	**-0.9**	**-0.9**	0.4	**0.9**	**1.0**							
Cu2	**-0.8**	0.6	0.2	**-0.8**	**-0.6**	-0.3	-0.3	**0.6**	**0.5**	0.2	0.0	0.0	-0.3	0.4	0.1	**1.0**						
Zn2	**-0.8**	0.5	-0.2	**-0.6**	**-0.5**	-0.3	-0.2	**0.6**	**0.6**	0.1	-0.1	-0.2	0.1	**0.7**	0.4	**0.9**	**1.0**					
Ni2	**-0.9**	0.4	0.2	**-0.9**	**-0.7**	-0.3	-0.5	0.5	**0.5**	0.1	-0.1	-0.2	-0.3	0.4	0.3	**1.0**	**0.9**	**1.0**				
Mg2	**-0.9**	0.5	0.0	**-0.8**	**-0.6**	-0.3	-0.3	**0.6**	**0.6**	0.1	-0.1	-0.2	-0.1	**0.6**	0.3	**1.0**	**1.0**	**1.0**	**1.0**			
Cr2	**-1.0**	0.3	0.0	**-0.9**	**-0.8**	-0.5	**-0.5**	0.4	0.4	-0.1	-0.3	-0.4	-0.2	**0.6**	0.4	**0.9**	**0.9**	**1.0**	**1.0**	**1.0**		
Sb2	**-1.0**	0.2	0.0	**-0.8**	**-0.8**	**-0.6**	**-0.5**	0.4	0.3	-0.1	-0.4	-0.4	-0.2	**0.6**	0.5	**0.9**	**0.9**	**0.9**	**1.0**	**1.0**	**1.0**	
Pb2	**-1.0**	0.1	0.0	**-0.8**	**-0.8**	**-0.7**	**-0.6**	0.3	0.2	-0.2	-0.5	**-0.5**	-0.3	**0.6**	**0.5**	**0.9**	**0.9**	**0.9**	**0.9**	**1.0**	**1.0**	**1.0**
	9.91	5.58	2.84	Eigenvalues																		
	52.16	29.39	14.92	% of explanation																		
	52.16	81.54	96.46	% total																		
	3.55	2.55	2.05	*Broken-Stick* eigenvalues																		

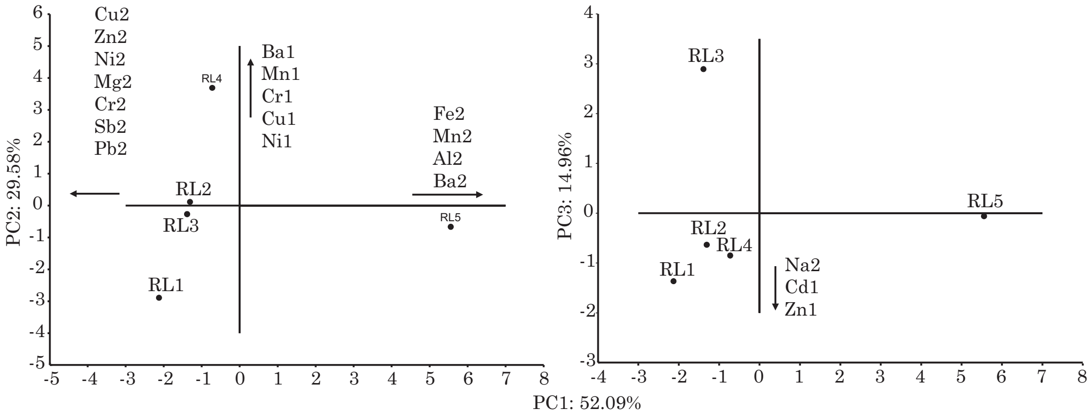

Figure 2. Scores of legal reserves obtained on major components and system variables (arrows) applied to the Pearson correlation matrix between metals of the soil samples [concentration transformed into log (x+1) to approximate normality conditions].

contamination could be identified by these components. Thus, it can be concluded that the natural TE concentration in this soil is greatly influenced by the source material and by the result of the combined action of geomorphological/climate processes or conditions, which make the TE levels found in this study specific. This fact confirms studies with materials of distinct origin and soil classes, in which variability of heavy metal levels was observed resulting from the pedogenic processes affecting these source materials (Vázquez & Anta, 2009).

RRV and Brazilian backgrounds

The background values and tolerance limits established for the elements Cd, Co, Cr, Cu, Ni, Pb, and Zn, were determined predominantly in samples of distroferric Red Latosol, distroferric Red Nitosol, Brown Latosol and eutroferric Red Argisol (Table 5), herein denominated group G1 (Fadigas et al., 2006). These studies demonstrated that the main physical, chemical and mineralogical characteristics of soils can influence the background values, including clay, Mn, Fe contents and cation exchange capacity (CEC).

Also, table 5 shows the results of backgrounds established in the State of Rio Grande do Sul with some TE levels determined in soil samples or sediments from preserved natural areas, the arithmetic mean TE values in 43 soil samples from Paraná determined by the geological service of Paraná - Mineropar (2005) and the values established by Resolution Nº 420 of Conama (2009) in which the soil quality is characterized by the PV and IV.

The backgrounds in this table were used for studies in analyses of anthropogenic enrichment of river and urban sediments (Poleto & Merten, 2008a,b; Poleto et al. 2009; Poleto & Cardoso, 2012), and the values differ substantially from the determined RRV. Thus, it is always essential to establish the background in order to draw conclusions in environmental contamination studies, since the specific properties of the pedogenetic formation or environmental factors can substantially affect the mobility and availability of TEs.

The RRV were close to the background presented by Fadigas et al. (2006). Also, the Latosol samples were undisturbed or nearly undisturbed by human activity. Only Cu reached levels close to the threshold established by these authors, but above the IV for agricultural soil indicated by Conama (2009), which can be justified by the fact that Toledo, PR, is located in the central portion of the third plateau of Paraná, with an area with peculiar anomalous Cu values (318.8 mg kg^{-1}) related to basic igneous rocks of the Serra Geral formation (Mineropar, 2005).

It was also observed that the RRV levels of the TEs Ba, Cr, Se, and U were lower than those cited by Mineropar (2005) and PV established by Resolution Nº 420 of Conama (2009). However, the other metals had similar or higher levels, since the geochemical survey was conducted with soil samples from unpreserved sites, unlike the legal reserves in this study.

RRV and guidelines

In this study, one of the concerns was the occurrence of enrichment of some TEs in the legal reserves, by the natural geological formation or through human actions. Therefore, the determined RRV (Table 6) were compared to the limit and intervention concentrations of the Dutch guideline, adopted by European countries in numerous pollution studies as a means of assessing contamination levels (Macklin et al., 2003; Lee et al., 2005) and also compared to the maximum allowable TE concentrations in sediments established by Conama (2004) for material disposal.

These data show a significant extrapolation for Cu, with levels requiring intervention, thus emphasizing the need for surveying the local background to be used in any study on TEs and the appropriate contamination levels in this environment. In this sense, Poleto & Gonçalves (2006) report that the specificity of each reference value is also clear when comparing the thresholds established by the Dutch with the Canadian guideline. The values found for studies in the Netherlands are very high when compared to the ones used in Canada, mainly due to mineralogical differences of each country, showing how extremely risky it is to take the studies produced in other regions or countries as a background of data for metals.

In this table, the RRV for Cr is on the probability threshold of causing adverse effects on freshwater biota

Table 5. Elements-trace concentration recommended by Conama, Paraná average values, G1 and their thresholds, background and RRV

Metal	Conama				Parana	G1 group	Threshold	Background		RRV$^{(3)}$
	PV$^{(1)}$	IV$^{(2)}$								
		Agricultural	Residential	Industrial				2008	2012	
	mg kg^{-1}									
Ba	150	300	500	750	170,84	n.a.	-			62,51
Cu	60	200	400	600	141,72	119	283			212,3
Cd	1,3	3	8	20	0,18	1	2	0,07	0,07	0,69
Co	25	35	65	90	23,84	29	44	19,00		n.a.
Cr	75	150	300	400	105,42	55	114			52,4
Mn					736,84	n.a.	-			916,4
Ni	30	70	100	130	34,16	35	92		4,89	30,26
Pb	72	180	300	900	23,21	19	35		31,30	17,46
Sb					0,74	n.a.	-			4,58
Se	5				0,53	n.a.	-			< 0,005
U					3,02	n.a.	-			< 0,01
Zn	300	450	1000	2000	75,26	79	149		47,45	82,14

(1) PV: prevention value. (2) IV: investigation value. (3) RRV: regional reference values (Toledo, PR). (4) n.a. (not analyzed).

Table 6. Comparison of RRV to the maximum allowable trace element concentrations for disposal of dredged material established by Conama 344/2004 and limits and intervention concentration of the Dutch guideline

Trace elemeny	RRV(1)	Conama 344/2004				Dutch Guideline(5)	
		Freshwater		Brackish saline water			
		Level 1	Level 2	Level 1(3)	Level 2(3)	Limit	Intervention
	mg kg^{-1}						
As	< 0.005	5.90(2)	17(2)	8.2	70	294	554
Ba	62.51	n.s.	n.s.	n.s.	n.s.	1,604	6,254
Cd	0.69	0.60(2)	3.5(2)	1.2	9.6	0.84	124
Cr	54.20	37.30(2)	90(2)	81.0	370	1,004	3,804
Cu	212.30	35.70(2)	197(2)	34.0	270	364	1,904
Hg	n.a.	0.17(2)	0.486(2)	0.15	0.71	0.34	104
Ni	30.26	18.00(4)	5.9(4)	20.9	51.6	354	2,104
Pb	17.46	35.00(2)	91.3(2)	46.7	218	854	5,304
Zn	82.14	123.00(2)	315(.2)	150.0	410	1,404	7,204

(1) RRV: regional reference values (Toledo, PR). (2) Environmental Canada (2002). (3) Long et al. (1995). (4) FDEP (1994). (5) Netherlands Government (2000). n.a.: not analyzed; n.s.: not specified.

(level I) and the Ni is on the probability threshold of causing adverse effects on both freshwater and saltwater biota (level I). The Cu concentration has harmful effects on freshwater (level I and II) or saltwater (level I). However, these effects are not considered threatening by Conama when considering the possibility that these soils will be deposited in riverbeds of this watershed in the form of sediments and may result from a dredging process.

It is noteworthy that the concentrations of the TEs As, Pb and Zn are presented in lower RRV than those of the aforementioned guideline (Table 6), thus, using only this guideline would allow TEs in higher concentrations than the levels naturally supported by this ecosystem. Thus, it is recommended that studies on environmental contamination be interpreted by criteria of the local geochemical survey (background), especially in view of the fact that natural sources of TEs may be considered harmful contaminants.

CONCLUSIONS

1. Recovery rates determined by the method of incomplete sample decomposition resulted in make the results more accurate and reproducible.

2. The coefficients of variation of RRV exceeded 10 % for most trace elements analyzed, resulting from the pedogenetic processes influencing the same source material.

3. The TE levels determined as RRV are, on average, higher than the reference values of quality for metals in soils of the State of São Paulo and also exceed the reference values proposed for 19 other Brazilian Latosols.

4. The correlation coefficients indicated the TEs with extreme values in the mineral matrix.

5. The PCA was ordered into three components that explained 96 % of the variability of the results and showed that there was no geogenic or anthropogenic source of contamination in the legal reserves.

6. The TE concentrations of the background of the eutroferric Red Latosols are below the guideline values, therefore these thresholds are permissible beyond the real tolerance level of the local ecosystem.

7. The background established in this study is indicated for TE monitoring in the watershed of Toledo PR or regions with similar characteristics.

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