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Background and Reference Values of Metals in Soils from Paraíba State, Brazil

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ABSTRACT: Soil contamination by heavy metals threatens ecosystems and human health. Environmental monitoring bodies need reference values for these contaminants to assess the impacts of anthropogenic activities on soil contamination. Quality reference values (QRVs) reflect the natural concentrations of heavy metals in soils without anthropic interference and must be regionally established. The aim of this study was to determine the natural concentrations and quality reference values for the metals Ag, Ba, Cd, Co, Cu, Cr, Mo, Ni, Pb, Sb and Zn in soils of Paraíba state, Brazil. Soil samples were collected from 94 locations across the state in areas of native vegetation or with minimal anthropic interference. The quality reference values (QRVs) were (mg kg^{-1}): Ag (<0.53), Ba (117.41), Cd (0.08), Co (13.14), Cu (20.82), Cr (48.35), Mo (0.43), Ni (14.44), Sb (0.61), Pb (14.62) and Zn (33.65). Principal component analysis grouped the metals Cd, Cr, Cu, Ni, Pb and Sb (PC1); Ag (PC2); and Ba, Co, Fe, Mn and Zn (PC3). These values were made official by Paraíba state through Normativa Resolution 3602/2014.

Keywords: geochemistry, soil pollution, micronutrients, trace elements.

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INTRODUCTION

Heavy metal concentrations in soils without anthropogenic influences are usually low and do not pose risks to humans or ecosystems (Alloway, 1990; Costa et al., 2004; Paye et al., 2010; Lu et al., 2012). However, agricultural, industrial and mining activities in recent decades have contributed to significant increases in the amount of these contaminants in the environment (Chen et al., 1991). In this context, environmental agencies need indicators that can be used as references for the continued evaluation of the impacts of anthropic activities. Consequently, guiding values of soil quality that enable the identification of contaminated areas and the assessment of the potential risks to ecosystems and human health need to be established (Soares, 2004; Biondi, 2010; Paye et al., 2010).

Taking into account the Brazilian territorial extent and soil heterogeneity, it is essential to assess the natural background concentrations of heavy metals at a regional scale to set up limits for distinction between natural concentrations and those derived from anthropogenic contamination. The Brazilian Environmental Council (Conama), through Resolution No. 420 of December 29, 2009, established that each state in the country must determine its own guiding values for heavy metal concentrations based on a set of soil samples that represent the local geomorphology, pedology and lithology. This was decided because the international values or those from other regions might result in erroneous interpretation regarding areas suspected of being contaminated. The Brazilian resolution establishes three types of guiding values: quality reference values (QRVs), which should be determined by each state, prevention values (PVs) and investigation values (IVs), which are established by the Conama Resolution (Conama, 2009) and are valid for the whole country.

The QRVs indicate the natural concentrations of chemical elements in soils without anthropic influence (Conama, 2009); however, as stated by Zhao et al. (2007), environments that are free from the influence of anthropic activity are becoming increasingly scarce. These values are established through statistical interpretation of natural concentrations in soil samples from a particular region, taking into account its main soil types. The PVs and IVs, on the other hand, are determined from human health-based risk analysis (Biondi et al., 2011a; Nascimento and Biondi, 2015).

The QRV determination regarding heavy metals in soils is well established in several countries (Chen et al., 1991; Kabata-Pendias and Pendias, 2000; Galuszka, 2007; Martínez-Lladó et al., 2008; Su and Yang, 2008; Bini et al., 2011; McDowell et al., 2013). In Brazil, few states have established their QRVs as required by Resolution 420; these include São Paulo (Cetesb, 2001), Minas Gerais (Copam, 2011), Paraíba (Copam, 2014), Pernambuco (Biondi et al., 2011a,b; CPRH, 2014) and Rio Grande do Sul (Fepam, 2014). The objective of this work was to determine the background concentrations and quality reference values (QRVs) of metals (Ag, Ba, Cd, Co, Cu, Cr, Fe, Mn, Mo, Ni, Pb, Sb and Zn) in soils of the state of Paraíba, aiming to help the state environmental agency to develop specific legislation for monitoring these elements in soils; and to assess the soil metal origins to prove their natural origin using multivariate analysis (MVA).

MATERIALS AND METHODS

The study area encompasses the entire state of Paraíba (06° 02’ to 08° 19’ S and 34° 45’ to 38° 45’ W), covering 56,438 km^2 (Brasil, 1972). An assessment analysis of the state soils (scale 1: 500,000) (Brasil, 1972) and geology (CPRM, 2002) maps was conducted, and 94 locations were selected for soil sampling such that the main geomorphological, pedological and geological compartments were represented (Figure 1). The geographical coordinates and altitudes of the sampling points were determined using a GPS device (Garmin Map 60C Sx). Municipalities, geographic coordinates, soil types, geological background and textural classes of the selected soils are shown in table 1.

Table 1. Identification, sampling locations (municipalities), geographical coordinates (Coord S/W), altitude (Alt), soil classes, and geological background of the studied soil

Ident.	Municipality	Coord S/W	Alt	Soil class(1)	Geological background(2)
			m		
1	Pitimbu	07°29’16”/34°49’13”	43	*Argissolo* (Typic Kandiudult)	S
2	Alhandra	07°24’21”/34°55’10”	69	*Latossolo* (Typic Hapludox)	S
3	Pedras de Fogo	07°21’55”/35°01’39”	131	*Neossolo Quartzarênico* (Typic Quarzipsament)	S
4	Pedras de Fogo	07°19’45”/34°56’43”	125	*Latossolo* (Typic Hapludox)	S
5	Conde	07°16’04”/34°53’01”	71	*Argissolo* (Typic Kandiudult)	S
6	Cabedelo	06°59’42”/34°53’01”	17	*Neossolo Quartzarênico* (Typic Quarzipsament)	S
7	Cabedelo	06°59’42”/34°49’41”	17	*Espodossolo* (Typic Haplorthod)	S
8	João Pessoa	07°03’52”/34°51’13”	70	*Neossolo Quartzarênico* (Typic Quarzipsament)	S
9	Mamanguape	06°51’43”/35°08’17”	15	NC	S
10	Santa Rita	06°59’03”/35°08’34”	146	*Argissolo* (Typic Kandiudult)	S
11	Santa Rita	07°00’53”/35°07’34”	194	*Neossolo Quartzarênico* (Typic Quarzipsament)	S
12	Sapé	07°02’60”/35°14’31”	146	*Argissolo* (Typic Kandiudult)	S
13	Itapororoca	06°51’27”/35°13’59”	95	*Luvissolo* (Aridic Haplustalf)	C
14	Baia da Traição	06°43’54”/34°57’09”	53	*Neossolo Quartzarênico* (Typic Quarzipsament)	S
15	Rio Tinto	06°48’09”/35°04’25”	21	*Gleissolo* (Typic Endoaquent)	S
16	Jacaraú	06°38’39”/35°16’05”	235	*Plintossolo* (Typic Udox)	C
17	Lagoa de Dentro	06°39’59”/35°23’10”	199	*Argissolo* (Typic Kandiudult)	C
18	Riachão	06°33’08”/35°40’04”	197	*Neossolo Litólico* (Lithic Ustortent)	C
19	Campo de Santana	06°29’56”/35°39’36”	334	*Neossolo Litólico* (Lithic Ustortent)	C
20	Solânea	06°41’29”/35°44’34”	332	*Neossolo Litólico* (Lithic Ustortent)	C
21	Solânea	06°41’28”/35°44’35”	327	*Cambissolo* (Oxic Ustropept)	C
22	Cassarengue	06°46’53”/35°48’17”	515	*Argissolo* (Typic Kandiudult)	C
23	Bananeiras	06°42’60”/35°38’14”	607	*Latossolo* (Typic Hapludox)	C
24	Areia	06°58’04”/35°44’11”	622	*Latossolo* (Typic Hapludox)	C
25	Areia	06°57’60”/35°44’10”	620	*Latossolo* (Typic Hapludox)	C
26	Alagoa grande	07°01’14”/35°37’41”	237	*Argissolo* (Typic Kandiudult)	C
27	Alagoinha	06°57’32”/35°33’10”	193	*Argissolo* (Typic Kandiudult)	C
28	Mulungu	06°58’41”/35°30’31”	140	*Argissolo* (Typic Kandiudult)	C
29	Gurinhém	07°08’47”/35°25’21”	123	*Neossolo Quartzarênico* (Typic Quarzipsament)	C
30	Itabaiana	07°19’00”/35°20’35”	110	*Argissolo* (Typic Kandiudult)	S
31	Mogeiro	07°19’07”/35°22’08”	128	*Neossolo Regolítico* (Typic Ustortent)	C
32	Mogeiro	07°16’41”/35°29’31”	159	*Neossolo Litólico* (Lithic Ustortent)	C
33	Fagundes	07°19’19”/35°46’32”	269	*Planossolo* (Typic Albaqualf)	C
34	Riachão do Bacamarte	07°15’02”/35°38’35”	148	*Neossolo Flúvico* (Typic Aquisalid)	C
35	Ingá	07°19’34”/35°37’42”	192	*Argissolo* (Typic Kandiudult)	C
36	Natuba	07°40’06”/35°36’53”	606	*Argissolo* (Typic Kandiudult)	C
37	Umbuzeiro	07°41’21”/35°39’02”	499	*Argissolo* (Typic Kandiudult)	C
38	Queimadas	07°22’34”/35°54’24”	430	*Vertissolo* (Chromic Haplustert)	C
39	Serra redonda	07°12’47”/35°39’33”	365	NC	C
40	Massaranduba	07°11’06”/35°43’08”	212	*Argissolo* (Typic Kandiudult)	C
41	Alagoa Nova	07°04’00”/35°42’28”	388	*Argissolo* (Typic Kandiudult)	C
42	Barra de Santa Rosa	06°44’08”/36°03’01”	474	*Planossolo* (Typic Albaqualf)	C
43	Cuité	06°28’34”/36°08’16”	669	*Latossolo* (Typic Hapludox)	C
44	Nova Floresta	06°27’41”/36°11’35”	670	*Latossolo* (Typic Hapludox)	S
45	Soledade	07°04’45”/36°19’44”	571	*Neossolo Litólico* (Lithic Ustortent)	C
46	Pocinhos	07°04’07”/36°03’06”	648	*Planossolo* (Typic Albaqualf)	C
47	Seridó	06°53’20”/36°23’52”	643	*Neossolo Quartzarênico* (Typic Quarzipsament)	C
48	Cubati	06°52’11”/36°22’10”	566	*Planossolo* (Typic Albaqualf)	C
49	Juazeirinho	07°02’51”/36°32’20”	581	*Planossolo* (Typic Albaqualf)	C
50	Junco do Seridó	07°01’50”/36°39’46”	584	*Argissolo* (Typic Kandiudult)	C
51	São Mamede	06°54’55”/37°01’51”	306	*Luvissolo* (Aridic Haplustalf)	C

Continue

Continuation

52	Taperoá	07°11’06”/36°49’39”	554	*Cambissolo* (Oxic Ustropept)	C
53	Livramento	07°19’18”/36°57’50”	614	*Cambissolo* (Oxic Ustropept)	C
54	Amparo	07°33’48”/37°00’55”	656	*Luvissolo* (Aridic Haplustalf)	C
55	Prata	07°42’47”/37°03’46”	615	*Luvissolo* (Aridic Haplustalf)	C
56	Monteiro	07°52’32”/37°05’44”	626	*Luvissolo* (Aridic Haplustalf)	C
57	Camalaú	07°50’51”/36°52’37”	574	*Luvissolo* (Aridic Haplustalf)	C
58	Sumé	07°42’22”/36°55’08”	553	*Planossolo* (Typic Albaqualf)	C
59	Serra Branca do Cariri	07°33’40”/36°40’39”	517	*Luvissolo* (Aridic Haplustalf)	C
60	São João do Cariri	07°26’35”/36°34’53”	492	*Luvissolo* (Aridic Haplustalf)	C
61	Gurjão	07°13’08”/36°26’53”	518	*Planossolo* (Typic Albaqualf)	C
62	Picuí	06°28’53”/36°18’46”	655	*Neossolo Litólico* (Lithic Ustortent)	C
63	Nova Palmeira	06°39’05”/36°24’20”	622	*Neossolo Regolítico* (Typic Ustortent)	C
64	Maturéia	07°14’22”/37°18’27”	760	*Cambissolo* (Oxic Ustropept)	S
65	Texeira	07°15’28”/37°16’14”	778	*Neossolo Regolítico* (Typic Ustortent)	C
66	Imaculada	07°24’14”/37°31’11”	746	*Neossolo Regolítico* (Typic Ustortent)	C
67	Juru	07°32’52”/37°50’04”	608	*Luvissolo* (Aridic Haplustalf)	C
68	Princesa Isabel	07°43’27”/38°00’18”	679	*Cambissolo* (Oxic Ustropept)	C
69	Princesa Isabel	07°43’20”/37°56’32”	759	*Argissolo* (Typic Kandiudult)	C
70	Tavares	07°37’06”/37°53’30”	706	NC	C
71	Santana dos Garrotes	07°27’03”/37°59’17”	346	*Neossolo Litólico* (Lithic Ustortent)	C
72	Olho d'Água	07°12’09”/37°45’09”	272	*Neossolo Litólico* (Lithic Ustortent)	C
73	Piancó	07°10’48”/37°54’45”	293	*Neossolo Litólico* (Lithic Ustortent)	C
74	Itaporanga	07°17’21”/38°07’40”	313	*Luvissolo* (Aridic Haplustalf)	C
75	Diamante	07°26’52”/38°17’14”	339	*Neossolo Litólico* (Lithic Ustortent)	C
76	Santana da Mangueira	07°31’26”/38°20’30”	379	*Neossolo Litólico* (Lithic Ustortent)	C
77	Conceição	07°31’49”/38°30’05”	432	*Cambissolo* (Oxic Ustropept)	C
78	Bonito de Santa Fé	07°15’39”/38°30’54”	626	*Argissolo* (Typic Kandiudult)	C
79	São José do Piranhas	07°08’25”/38°30’25”	375	*Luvissolo* (Aridic Haplustalf)	C
80	Cajazeiras	06°51’43”/38°31’51”	276	*Luvissolo* (Aridic Haplustalf)	C
81	São José do Rio do Peixe	06°41’47”/38°28’41”	296	NC	S
82	Triunfo	06°35’26”/38°34’30”	306	*Planossolo* (Typic Albaqualf)	S
83	Uiraúna	06°33’54”/38°24’44”	309	*Argissolo* (Typic Kandiudult)	C
84	Sousa	06°46’14”/38°17’12”	232	*Vertissolo* (Chromic Haplustert)	S
85	Sousa	06°45’44”/38°17’16”	241	*Planossolo* (Typic Albaqualf)	S
86	Catolé do Rocha	06°20’06”/37°42’36”	276	*Argissolo* (Typic Kandiudult)	C
87	Belém do Brejo do Cruz	06°13’32”/37°32’15”	207	*Argissolo* (Typic Kandiudult)	C
88	São Bento	06°25’43”/37°27’09”	174	*Luvissolo* (Aridic Haplustalf)	C
89	Paulista	06°34’45”/37°35’39”	180	*Luvissolo* (Aridic Haplustalf)	C
90	Pombal	06°43’07”/38°01’08”	282	*Argissolo* (Typic Kandiudult)	C
91	Malta	06°52’56”/37°31’53”	294	*Argissolo* (Typic Kandiudult)	C
92	São José do Espinharas	06°50’27”/37°23’57”	238	*Luvissolo* (Aridic Haplustalf)	C
93	Patos	02’17”/37°20’29”	280	*Luvissolo* (Aridic Haplustalf)	C
94	Santa Terezinha	07°04’60”/37°25’02”	306	*Luvissolo* (Aridic Haplustalf)	C

(1) Soil classes in according to Santos et al. (2013) (Soil Survey Staff, 2014); (2) S: sedimentary rock; C: crystalline basement; NC: not classified. Ident.: soil identification.

A composite sample was formed from 10 samples collected at each sampling site, in areas of native vegetation, with minimal or no anthropic interference, using a stainless steel Dutch auger at a depth of 0.0-0.2 m. Thereafter, the samples were air dried, disaggregated, homogenized and sieved through a nylon sieve with a 2.0 mm mesh (ABNT No. 10).

The following physical and chemical analyses of the samples were performed: particle size (Donagema et al., 2011), pH in water (1:2.5), potential acidity (H+Al), P, exchangeable cations (Na^+, K^+, Ca^{2+}, Mg^{2+} and Al^{3+}) and organic carbon (OC), according to Santos et al. (2009). The exchangeable cation results were used to calculate the sums of bases

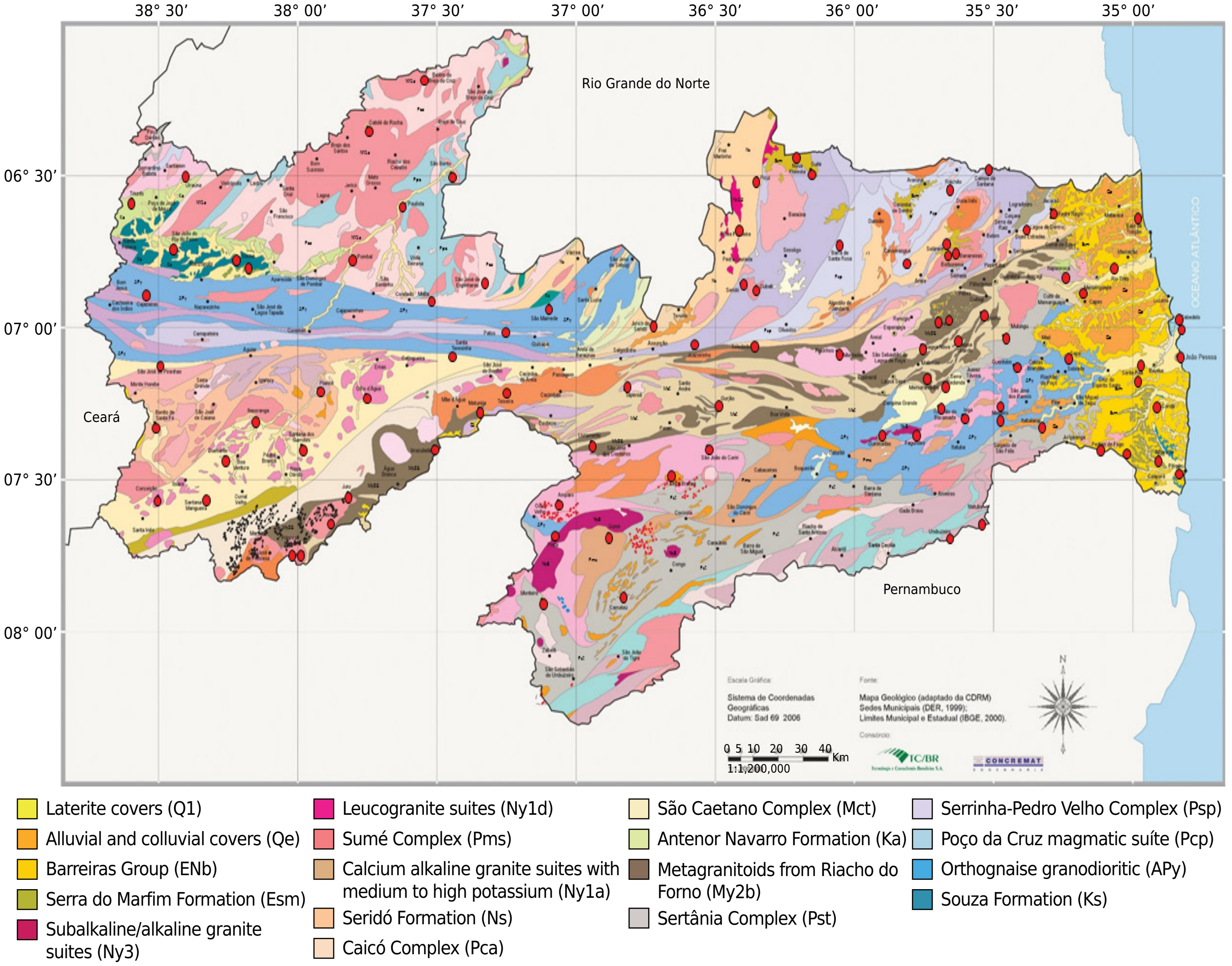

Figure 1. Geological map of Paraíba state (Brazil) showing the sampling locations (CPRM, 2002, modified).

(SB), the total (T) and effective (t) cation exchange capacity, base saturation (V) and Al saturation (m). All analyses were performed in triplicate (Table 2).

To extract the metals Ag, Ba, Cd, Co, Cu, Cr, Fe, Mn, Mo, Ni, Pb, Sb and Zn from the soil samples, the 3051A digestion method (Usepa, 1998) was used. In this procedure, sample aliquots were ground in agate mortar, homogenized and passed through a stainless steel 0.3 mm mesh sieve (ABNT 50). Thereafter, 1 g of the powdered samples was transferred to high-pressure teflon tubes to which 9 mL of nitric acid 65 % (v/v) and 3 mL of hydrochloric acid 37 % (v/v) were added, both of which were of high analytical purity (Merck PA). The digestion was performed in a closed system using a microwave oven (Mars Xpress, CEM Corporation, Matthews, NC, USA); the temperature was increased to 175 °C over a time period of 8′40″, which was maintained for a further 4′30″. After cooling, the extracts were transferred to 25 mL certified flasks (NBR ISO/IEC), which were filled to volume with ultrapure water. Then, the extracts were filtered through slow filter paper (Macherey Nagel®). These analyses were performed in triplicate in parallel with blank tests.

The calibration curves for determining the metal concentrations were prepared from standard solutions of 1000 mg L^{-1} (Titrisol®, Merck) using ultrapure water for dilution. The metal concentrations were determined using inductively coupled plasma optical emission spectrometry (ICP-OES) with an insertion system via an automatic sampler

Table 2. Selected chemical and physical characteristics of the Paraíba State soil samples studied (n = 94)

Characteristic	Mean	Median	Minimum	Maximum	Standard deviation
pH(H_2O)	5.7	5.8	3.9	7.2	0.72
H+Al (cmol$_c$ dm^{-3})	3.67	3.04	0.21	15.88	2.54
Al^{3+} (cmol$_c$ dm^{-3})	0.27	0.10	0.05	2.80	0.42
Na^+ (cmol$_c$ dm^{-3})	0.14	0.08	0.02	1.69	0.21
K^+ (cmol$_c$ dm^{-3})	0.36	0.33	0.02	1.02	0.21
Ca^{2+} (cmol$_c$ dm^{-3})	4.6	3.7	0.2	25.8	4.4
Mg^{2+} (cmol$_c$ dm^{-3})	2.9	2.2	0.1	21.8	3.0
SB (cmol$_c$ dm^{-3})	8.1	6.4	0.6	48.5	7.3
t (cmol$_c$ dm^{-3})	8.3	6.6	1.7	48.6	7.2
T (cmol$_c$ dm^{-3})	11.7	9.8	3.7	51.5	7.08
V (%)	63.9	71.0	8.3	98.0	22.7
m (%)	7.8	1.5	0.2	69.9	14.6
OC (g kg^{-1})	11.9	9.8	2.3	39.6	6.6
Sand (g kg^{-1})	685	727	152	932	168
Silt (g kg^{-1})	125	96	19	485	102
Clay (g kg^{-1})	190	162	40	465	98

pH in water, relation 1;2.5, v/v; H+Al: extractor 0.5 mol L^{-1} calcium acetate at pH 7.0; Ca^{2+}, Mg^{2+}, Al^{3+}: extractor 1 mol L^{-1} KCl; K, Na: extractor Mehlich-1; SB: sum of bases; t: cation exchange capacity effective; T: cation exchange capacity in pH 7,0; V: base saturation; m: aluminum saturation; OC: organic carbon, Walkley-Blake method; Sand, silt, clay: pipette method.

(AS 90 plus). The quality control of the method used for the analysis of the metals in the soil samples was carried out using the values of metals in soil samples certified by the NIST (National Institute of Standards and Technology) (NIST, 2002), SRM 2711, and Montana soil (Moderately elevated trace elements concentrations).

The analytical results were evaluated through univariate statistical methods and multivariate techniques. After the anomalies were removed (based on a box-plot construction as recommended by Conama (2009), the QRVs were established for each metal based on the 90th percentile of the sample universe. A univariate procedure (mean, median, minimum and maximum values and standard deviation) was used to characterize the physical and chemical properties of the samples. The multivariate technique adopted was factorial analysis, where one of the factors with eigenvalues greater than 1.0 was extracted by principal components and the factorial axes were rotated using the Varimax method. All statistical procedures were performed using Statistica 7.0 software.

RESULTS AND DISCUSSION

Heavy metal recovery in the certified sample

The digestion method 3051A, which uses HNO_3 and HCl, determines the pseudo-total or "environmentally available" concentrations of heavy metals. In this context, NIST recommends the comparison of methods that do not use HF (3050, 3051 and its updates), with recoveries based on leachate values (Biondi et al., 2011a).

The recovery rates of the certified reference sample (SRM2711 Soil Montana), based on the leachate, were generally satisfactory for all heavy metals, varying from 73 to 113 % (Table 3). Lower recoveries were found for Zn (73 %) and Ni (85 %). These results confirm those found by Biondi et al. (2011a,b) and Preston et al. (2014), and ensure the quality and reliability of the results found in this analysis.

Table 3. Recovery of heavy metals in the reference soil (SRM 2711 – Montana) based on the Usepa method 3051A (n = 4)

Metal	Determined value	Certified value (NIST)(1)	Recovery(2)	Leaching value (NIST)	Leaching-based recovery(3)
	mg kg^{-1}		%		
Ag	4.75	4.63 ± 0.39	95	86	110
Ba	169.93	726 ± 38	25	28	88
Cd	38.31	41.7 ± 0.25	92	96	96
Co	7.44	10	74	82	90
Cu	111.54	114 ± 2	100	88	113
Cr	20.61	47	44	43	102
Fe	20,273.75	28,900 ± 600	72	76	94
Mn	484.05	638 ± 28	79	77	103
Mo	0.00	1.6	0	*	*
Ni	12.86	20.6 ± 1.1	66	78	85
Pb	954.88	1162 ± 31	84	95	89
Sb	13.81	19.4 ± 1.8	78	*	*
Zn	224.29	350.4 ± 4.8	65	89	73

(1) NIST: National Institute of Standards and Technology; (2) % Recovery = (determined value/certified value) × 100; (3) % leaching-based recovery = (recovery/leaching value) × 100; *: values not determined by the NIST (2002).

Establishing quality reference values (QRVs)

The graphical box-plot was used to assess the need to exclude anomalous values (outliers and extreme outliers) from the data matrix to establish the QRV of each metal. The elements Ni, Cd, Sb, Cu and Cr (Table 4) had the most anomalous data, indicating that the distribution of these metals in the soils from Paraíba state is more heterogeneous compared with the other metals, and that there are regions where the concentrations of these metals are higher than the average values. Different results were found for Rio Grande do Norte soils, where anomalous values were higher for the metals Ba, Cr, Fe, Sb and Zn (Preston et al., 2014).

The Brazilian legislation (Conama Resolution No. 420/2009) states that QRVs can be established based on the 75th or 90th percentiles of the sample universe, after removing the anomalies. In São Paulo (Cetesb, 2001), Minas Gerais (Caires, 2009), Mato Grosso and Rondônia (Santos and Alleoni, 2013) and Rio Grande do Norte (Preston et al., 2014) the QRVs were established using the 75th percentile, whereas this study considered the 75th and 90th percentiles. However, the state environment agency has decided to use data from the 90th percentile to establish the QRVs for Paraíba soils; these values were 22 to 46 % higher than those based on the 75th percentile (Table 4). For comparison with studies from other Brazilian states, only data from the 75th percentile of the Paraíba soils were used.

In general, the QRVs from this study were lower than those reported by Cancela et al. (2004) for Galicia soils in Spain: Cd (2.8 mg kg^{-1}), Cu (42.8 mg kg^{-1}), Cr (79.4 mg kg^{-1}), Mn (1733 mg kg^{-1}), Zn (112.5 mg kg^{-1}) and Fe (49.7 g kg^{-1}). The Cd background value in Beijing, i.e., 0.12 mg kg^{-1} (Chen et al., 2004) and Antarctic soils, i.e., 0.17 mg kg^{-1} (Lu et al., 2012), was also higher than the QRV for Cd found in this study (Table 4). A high cadmium concentration is found in soils originating from mafic rocks and is restricted to soils formed from gneiss, arenite and sediments from the Tertiary (Ross, 1994), a prevailing condition in the state of Paraíba.

The QRVs of most of the metals were generally lower than the values reported in other regions of Brazil (Table 5). The Ag and Mo concentrations were below the detection limit (<DL) of the method for approximately 92 % of the evaluated soil samples, confirming the results found by Fabricio Neta (2012) for Fernando de Noronha soils. In these cases, the <DL values for Ag (0.53 mg kg^{-1}) and Mo (0.43 mg kg^{-1}) were used as their QRVs (Conama, 2009).

Table 4. Background concentrations (Mean, Median, and Maximum values) and quality reference values (QRVs) for heavy metals in soils of Paraíba state, and prevention and investigation values based on Conama (2009)

Metal	Mean	Median	Maximum	SD	n(1)	P(75)	P(90)	PV	IV
Ag (mg kg^{-1})	0.04	<DL	1.41	0.17	0	<0.53	<0.88	0.25	25
Ba (mg kg^{-1})	60.85	46.34	336.25	60.78	4	87.96	117.41	150	300
Cd (mg kg^{-1})	0.06	0.04	0.84	0.12	7	0.06	0.08	1.3	3
Co (mg kg^{-1})	5.97	3.57	44.89	7.27	3	7.93	13.14	25	35
Cu (mg kg^{-1})	10.25	5.75	81.98	12.33	6	11.22	20.82	60	200
Cr (mg kg^{-1})	28.14	15.56	266.08	38.31	5	28.81	48.35	75	150
Fe (g kg^{-1})	14.31	11.36	51.61	10.86	4	18.74	24.07	*	*
Mn (mg kg^{-1})	268.33	199.33	2,608.75	336.67	3	350.83	504.08	*	*
Mo (mg kg^{-1})	0.01	<DL	0.43	0.06	0	<0.24	<0.33	30	50
Ni (mg kg^{-1})	12.22	4.39	156.73	22.79	11	9.12	14.44	30	70
Pb (mg kg^{-1})	8.11	7.10	33.00	5.46	3	10.01	14.62	72	180
Sb (mg kg^{-1})	0.42	0.24	4.26	0.67	7	0.39	0.61	2	5
Zn (mg kg^{-1})	16.97	15.33	44.43	11.01	0	23.46	33.65	300	450

<DL: detection limit; SD: standard deviation; n(1): number of anomalous values excluded through box-plot analysis; P(75): QRV based on the 75th percentile; P(90): QRV based on the 90th percentile; *: Values not determined by Conama (2009).

Table 5. Quality reference values (QRVs) for heavy metals in soils of Brazilian states and the archipelago of Fernando de Noronha calculated from the 75th percentile

Metal	SP(1)	MG(2)	MT and RO(3)	RN(4)	PB(5)	Fernando de Noronha(6)
Ag (mg kg^{-1})	0.25	-	-	0.88	<0.53	-
Ba (mg kg^{-1})	75	171.43	-	58.91	87.96	834.88
Cd (mg kg^{-1})	<0.5	1.01	<0.3	0.10	0.06	-
Co (mg kg^{-1})	13	17.50	21.30	15.41	7.93	19.61
Cr (mg kg^{-1})	40	86.59	44.80	30.94	11.22	266.13
Cu (mg kg^{-1})	35	13.22	20.60	13.69	28.81	41.49
Fe (g kg^{-1})	-	83.07	-	-	18.74	-
Mn (mg kg^{-1})	-	446.91	-	-	350.83	-
Mo (mg kg^{-1})	<4.00	-	-	-	<0.24	-
Ni (mg kg^{-1})	13	23.04	2.10	19.84	9.12	58.75
Pb (mg kg^{-1})	17	15.80	9.00	16.18	10.01	-
Sb (mg kg^{-1})	<0.5	-	-	0.18	0.39	5.96
Zn (mg kg^{-1})	60	31.04	3.00	23.85	23.46	117.58

(1) Cetesb (2001); (2) Copam (2011); (3) Santos and Alleoni (2013); (4) Preston et al. (2014); (5) This study; (6) Fabrício Neta (2012).

The QRVs for the Paraíba soils were lower than those reported for São Paulo soils (Cetesb, 2001), except for Ba (Table 5), which was also higher than that reported by Preston et al. (2014) for Rio Grande do Norte soils, indicating the richness of this element in Paraíba soils. However, the QRV for Ba was lower than that reported by Fabrício Neta (2012) for Fernando de Noronha soils from volcanic origin in the archipelago (Table 5), which exceeded the QRV for an industrial scenario (750 mg kg^{-1}) suggested by Conama. Hence, there is a need for legislation based on cases that are considered exceptions, which are currently treated as anomalies but actually represent a legitimate pedological difference. Furthermore, Biondi et al. (2011b) suggested that areas without anthropic activity with elevated Ba concentrations require a thorough examination to evaluate its mobility and bioavailability, which may aid in verifying the potential risk of using these areas.

The values reported by Caires (2009) for all metals analyzed in Minas Gerais (MG) soils were higher than the QRVs found for the Paraíba soils (Table 5). This difference can be explained by the nature of the source material of the MG soils. The MG Iron Quadrangle is recognized worldwide for its geochemical anomalies and mineral deposits, while the MG Triangle is noted for its mafic volcanic processes (Carvalho Filho et al., 2011). The QRVs found in Paraíba were higher than the values reported by Santos and Alleoni (2013) for Mato Grosso (MT) and Rondonia (RO) soils with respect to Ni (2.1 mg kg^{-1}), Pb (9.0 mg kg^{-1}) and Zn (3.0 mg kg^{-1}) soil concentrations, but were lower than the Co (21.3 mg kg^{-1}), Cu (20.6 mg kg^{-1}) and Cr (44.8 mg kg^{-1}) concentrations (Table 5).

The QRVs found in Paraíba were also higher than the values reported by Paye et al. (2010) for soils of the state of Espírito Santo (ES) with respect to Mn (131.69 mg kg^{-1}) and Pb (<4.54 mg kg^{-1}), but were lower for Co (10.21 mg kg^{-1}) and Cr (54.13 mg kg^{-1}), and similar for Ni (9.12 mg kg^{-1} for Paraíba and 9.17 mg kg^{-1} for Espírito Santo). The low natural concentration of heavy metals found in Espirito Santo soils is due to the source material (Precambrian crystalline rocks and Tertiary and Quaternary sediments) (Paye et al., 2010), which is similar to the source materials of the Paraíba soils because the Paraíba subsoil consists mostly of Precambrian crystalline rocks that cover approximately 80 % of this area (CPRM, 2002). Therefore, the lower metal concentration found in these states confirms that the source material from crystalline and sedimentary rocks has a considerable influence on the low concentrations of the metals in these soils.

On the soils of Rio Grande do Norte state, Preston et al. (2014) reported QRVs higher than those found in Paraíba soils for most of the studied metals, except for Ba (58.91 mg kg^{-1}) and Sb (0.18 mg kg^{-1}). The differences in the QRVs for the heavy metal concentrations between the Paraíba soil and the soil from other regions of Brazil are mainly due to differences in the parent material composition (De Temmerman et al., 2003; Bini et al., 2011; Tume et al., 2011). It must be kept in mind, however, that the distribution of heavy metals in soils can be highly variable at the surface and at depth as a result of the heterogeneity of parent materials as well as other factors that control pedogenesis (Martínez-Lladó et al., 2008). For example, the natural concentrations of heavy metals cannot be directly related to the soil parent material because pedogenetic processes appear to be a decisive factor in Fe, Mn, Ba, Cr, Zn, Pb, Cd, As and Hg concentrations, whereas Cu, Ni and Co can be directly related to the parent material (Biondi, 2010).

Multivariate analysis

The data were subjected to a Pearson correlation matrix and principal component analysis (PCA) to select those studied characteristics that best represented the Paraíba soils. The Pearson correlation allowed examination of the data using multivariate analysis, which indicated significant ($p<0.01$) and positive correlations between most of the analyzed variables, except for Mo (Table 6). The variables must have a substantial number of correlations equal to or higher than 0.30 to ensure the existence of true factors (Hair Júnior et al., 2009). The principal component analysis is a technique that allows examination of the correlations between variables and the identification and elimination of those that contribute little to the overall variation (Mardia et al., 1979). Thus, Mo was excluded from later analyses.

After the exclusion of Mo, the data matrix was composed of 12 variables and 94 soil samples that were subjected to PCA, which generated 12 principal components (PC), each with a decreasing percentage of the initial data variability. It is noteworthy that the PCA was performed using standardized data (zero mean and variance equal to 1); thus, only components with eigenvalues greater than the unit are significant. Therefore, the heavy metals could be grouped into a model of three components that explained 81.89 % of the total variability of the data (Figure 2). This matrix demonstrates that Cd, Cr, Cu, Ni, Pb and Sb were associated with the first component (PC1); the second component (PC2) included only Ag, and the third component (PC3) grouped the metals Ba, Co, Fe, Mn and Zn.

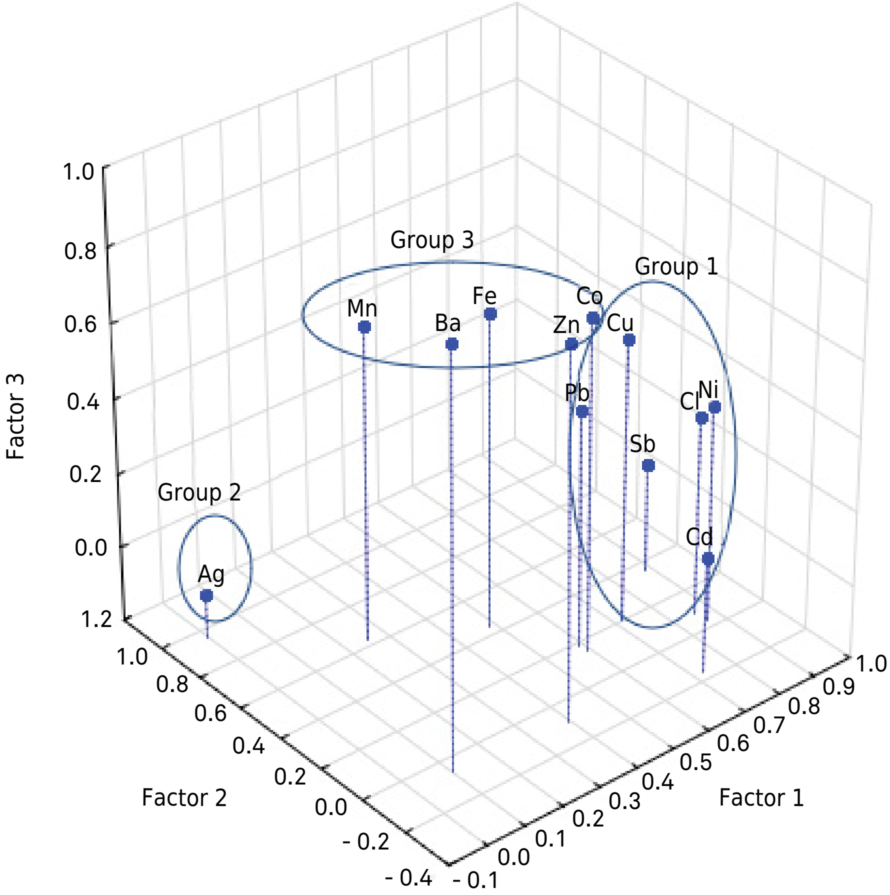

Figure 2. Graphical display of the principal components influencing the heavy metal concentrations in soils.

Table 6. Pearson correlation coefficients between heavy metal concentrations in soils of Paraíba

Metal	Ag	Ba	Cd	Co	Cu	Cr	Fe	Mn	Mo	Ni	Pb	Sb	Zn
Ag	1.00	-0.07^{ns}	-0.05^{ns}	0.05^{ns}	0.15^{ns}	0.04^{ns}	0.35**	0.51**	-0.05^{ns}	-0.03^{ns}	0.11^{ns}	0.30**	-0.12^{ns}
Ba	-0.07^{ns}	1.00	0.29**	0.68**	0.57**	0.41**	0.58**	0.56**	-0.20^{ns}	0.44**	0.36**	0.17^{ns}	0.68**
Cd	-0.05^{ns}	0.29**	1.00	0.35*	0.62**	0.48**	0.28**	0.20**	-0.03^{ns}	0.53**	0.49**	0.53**	0.43**
Co	0.05^{ns}	0.68**	0.35**	1.00	0.83**	0.83**	0.78**	0.72**	-0.19^{ns}	0.88**	0.52**	0.65**	0.70**
Cu	0.15^{ns}	0.57**	0.62**	0.83**	1.00	0.80	0.80**	0.70**	-0.17^{ns}	0.84**	0.66**	0.69**	0.68**
Cr	0.04^{ns}	0.41**	0.48**	0.83**	0.80**	1.00	0.70**	0.45**	-0.11^{ns}	0.96**	0.54**	0.81**	0.54**
Fe	0.35**	0.58**	0.28**	0.78**	0.80**	0.70**	1.00	0.73**	-0.17^{ns}	0.66**	0.67**	0.66**	0.68**
Mn	0.51**	0.56**	0.20**	0.72**	0.70**	0.45**	0.73**	1.00	-0.17^{ns}	0.50**	0.54**	0.50**	0.53**
Mo	-0.05^{ns}	-0.20^{ns}	-0.03^{ns}	-0.19^{ns}	-0.17^{ns}	-0.11^{ns}	-0.17^{ns}	-0.17^{ns}	1.00	-0.11^{ns}	-0.17^{ns}	-0.05^{ns}	-0.23^{ns}
Ni	-0.03^{ns}	0.44**	0.53**	0.88**	0.84**	0.96**	0.66**	0.50**	-0.11^{ns}	1.00	0.54**	0.80**	0.57**
Pb	0.11^{ns}	0.36**	0.49**	0.52**	0.66**	0.54**	0.67**	0.54**	-0.17^{ns}	0.54**	1.00	0.65**	0.71**
Sb	0.30**	0.17^{ns}	0.53**	0.65**	0.69**	0.81**	0.66**	0.50**	-0.05^{ns}	0.80**	0.65**	1.00	0.41**
Zn	-0.12^{ns}	0.68**	0.43**	0.70**	0.68**	0.54**	0.68**	0.53**	-0.23^{ns}	0.57**	0.71**	0.41**	1.00

**: significant at 1 %; ^{ns}: not significant.

The first component (PC1) explained more than 59 % of the total variance and represented some of the metals that are most commonly associated with soil contamination, such as Cd and Pb (Figure 2). The second component (PC2), which accounted for 12 % of the total variance, comprised only Ag. This was probably due to the very low concentrations of this metal compared with the other studied elements. The third component (PC3) explained approximately 10 % of the total variance and comprised some of the elements with the highest concentrations in soil, such as Ba, Fe, Mn and Zn. The results of the PCA, the relatively low natural concentrations (Table 4) and the significant correlations between metals (Table 6) confirm the predominant natural source of these elements in the soil and the suitability of using this data set for the development of quality reference values.

CONCLUSIONS

The analysis of the background concentrations of heavy metals in Paraíba state soils generated quality reference values that were lower than those reported for other states in Brazil.

The QRVs based on the 90th percentile for the Paraíba soils were as follows (mg kg^{-1}): Ag (<0.53), Ba (117.41), Cd (0.08), Co (13.14), Cu (20.82), Cr (48.35), Mo (0.43), Ni (14.44), Sb (0.61), Pb (14.62) and Zn (33.65).

The principal component analysis, which grouped the metals Cd, Cr, Cu, Ni, Pb and Sb (PC1); Ag (PC2); and Ba, Co, Fe, Mn and Zn (PC3), suggests the natural origin of these elements in the studied soils.

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