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Natural Fertility and Metals Contents in Soils of Rio Grande do Sul (Brazil)

Daiana Althaus[(1)*], Clesio Gianello[(1)], Marino José Tedesco[(1)], Kelly Justin da Silva[(2)], Carlos Alberto Bissani[(1)] and Regina Felisberto[(3)]

[(1)] Universidade Federal do Rio Grande do Sul, Departamento de Solos, Porto Alegre, Rio Grande do Sul, Brasil.
[(2)] Universidade Federal do Paraná, Departamento de Genética, Curitiba, Paraná, Brasil.
[(3)] Instituto Federal de Educação, Ciência e Tecnologia do Rio Grande do Sul, *Campus* Porto Alegre, Porto Alegre, Rio Grande do Sul, Brasil.

ABSTRACT: The parent geological materials and formation factors influence the chemical, physical, and mineralogical properties and composition of the soil. Therefore, the aims of this study were to determine the chemical and some physical and mineralogical properties of the soil useful for agricultural practice; to determine the natural contents of the semitotal metals in soils of the state of Rio Grande do Sul (Brazil); and to suggest use of the quality reference values (QRVs) in accordance with Resolution 420/2009 of the National Commission for the Environment (Conama). To determine some soil properties useful for agricultural, 254 surface soil samples from areas without known human influence (native grasslands or forests) were analyzed according to the methodology used by the soil testing laboratories of the state of Rio Grande do Sul. In addition, the semitotal heavy metal (Cd, Co, Cr, Cu, Ni, Pb, V, and Zn) contents of the soil were determined by the Usepa 3050B method and Hg was determined through an adaptation of the Usepa 7471 method. The results were studied in five soil groups from the state of Rio Grande do Sul according to soil parent materials: (1) basalt (volcanic rocks) of the Plateau region, (2) crystalline rocks (granite, schists, etc.) of the Southern Shield, (3) pelitic rocks (siltstones, mudstones, etc.) of the Peripheral Depression, (4) sandstones (sedimentary) of the Central Plains, and (5) sediments (unconsolidated) of the Coastal Plains. The properties for agricultural use of these soils were compared using the criteria adopted by the current fertilizer recommendations for the state. Multivariate analysis was used to study metals contents. Average values of available P contents were low in all soil groups; however, average values were high in several soil groups for available K. Averages of total acidity and cation exchange capacity were higher in Group 1 soils. The average values of extractable Zn, Cu, and S were high in all soils. Averages of Fe oxides were higher in the soils formed over basalt than in the other soils. Average metal (Cd, Co, Cr, Cu, Ni, Pb, V, and Zn) contents were higher in Group 1 soils than in the other soil groups (2 to 5). For Hg, however, average values were similar for all soil groups. The Spearman correlation coefficients were positive and highest among the metals (except for Cd and Hg) and the clay, Fe_d, and extractable Cu soil properties. Another high positive correlation coefficient was found between semitotal Cu and Zn contents and organic carbon. The QRVs for Cd, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn, determined according to Conama Resolution 420/2009, followed the same trend as the average metals contents.

Keywords: native soils, chemical properties, heavy metals, quality reference values.

*** Corresponding author:**
E-mail: daiana_althaus@yahoo.com.br

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INTRODUCTION

Soils develop over geological parent materials as a result of several factors, such as climate, position in the landscape, and biotic activity over long periods of time. In the southernmost state of Brazil (Rio Grande do Sul - RS) are very ancient crystalline rocks (such as granites, schists, etc.), sedimentary rocks (siltstones, claystones, sandstones), more recent volcanic rocks (basalt), and late unconsolidated deposited materials (sediments). These materials influence the soils properties and the content of elements such as heavy metals. Knowledge of the origin and distribution of geological materials contributes to a better understanding of the occurrence of various types of soils in RS. The geological parent materials are distributed according to the geomorphological provinces of RS, which are the Southern Shield, Peripheral Depression, Plateau, and Coastal Plains (Streck et al., 2008).

The first comprehensive description, classification, and mapping of RS soils was presented by Lemos et al. (1973) and revised according to the Brazilian Soil Classification System by Streck et al. (2008). In those studies, 74 soil mapping units were presented, along with several intermixed formations.

The first characterization of undisturbed soil (with no anthropogenic influence) for agricultural purposes was that presented by Lemos et al. (1973). Several soil surveys were conducted after that, starting with the study of Porto (1970), using data from the soil testing laboratories that operated as a support for the RS program that started in 1966, which aimed to increase crop yield (mainly wheat, corn, and soybeans). The latest state soil survey, published by Rheinheimer et al. (2001), included the results of 168,000 soil samples taken throughout the state. In these surveys, the data of pH(H_2O), available P and K, total acidity (SMP method), organic matter, and clay content were studied. The methods described by Mielniczuk et al. (1969) reviewed by Tedesco et al. (1995) were used for soil testing. The surveys conducted by Porto (1970) and Rheinheimer et al. (2001) mostly used samples of soils under cultivation.

Up to 1983, available Ca and Mg were not routinely determined in the soil testing laboratories of RS since most of the soils had high total acidity and therefore required liming, which increased these contents.

In 1982 and 1983, more detailed soil sampling was conducted in RS to characterize soil fertility in order to establish the soil samples collection of the Soil Science Department of the School of Agronomy at the Federal University of Rio Grande do Sul (UFRGS). These samples were described by location, mapping unit, vegetation, land use, soil depth, and chemical analysis for crop production (routine determinations) and summarized in a report to the sponsors of this research [UFRGS and the Studies and Projects Funding Agency (Finep)] by Volkweiss et al. (1983). Approximately one thousand samples were taken. Of these, about one quarter were collected from areas without known human influence (native grasslands or forests). These samples were used to characterize the native state of the soils of RS, in general and by physiographic region, from the standpoint of agricultural practice (plant macro- and micronutrients), heavy metals contents, or for other purposes.

Increasing ecological concerns over soil quality and soil use for disposal of residues (domestic and industrial), starting in the 1980s, led several Brazilian state agencies to study and propose soil quality standards, such as contents of heavy metals or other substances in soils. In RS, maximun levels of tannery residues (containing Cr) were established (Rodrigues et al., 1993). In the state of São Paulo, the Environmental Agency of the State of São Paulo (Cetesb) presented guidelines for soil and groundwater quality (Cetesb, 2001, 2005), which were later adopted by the National Environment Commission (Conama) (Conama, 2009).

The semitotal contents of some metals (Cd, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn) from the samples of undisturbed surface soils of RS in the UFRGS Soil Bank were presented by Althaus et al. (2014). The State Environmental Protection Foundation (Fepam) later adopted the QRVs with some adaptations that were required by the different properties of the soils of the state of RS (Fepam, 2014).

The aims of this study were to determine the chemical and some physical and mineralogical properties of the soil useful for agricultural practice; to determine the natural contents of the semitotal metals Cd, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn in soils of the state of Rio Grande do Sul; and to suggest use of the quality reference values (QRVs) in accordance with Resolution 420/2009 of the Conama.

MATERIALS AND METHODS

Soil samples

At the end of 1983, a soil sample collection was established at the Federal University of Rio Grande do Sul through collection of approximately 1,000 samples representing the 74 soil mapping units described by Lemos et al. (1973) in the five geomorphological regions of the state (Streck et al., 2008).

Each sample was characterized by location, soil mapping unit, vegetation, slope, parent material, and soil use. The samples taken from the top layer (0.00-0.20 m depth) were air dried, ground to pass through a 2 mm sieve (ABNT 10), and kept in tightly closed PVC jars.

In this soil collection, 254 samples were collected in areas without previous apparent human activity (native grassland or forests), and they were used in this study. The soil samples were classified into five soil groups, according to their parent materials (Table 1). The location of the soil groups in the state is shown in figure 1.

Chemical, physical, and mineralogical characterization of the soils for agricultural use

In the soil samples, particle size, pH(H_2O), total acidity (H+Al), available P and K, extractable S, total nitrogen, and organic matter were determined. The results were summarized by Volkweiss et al. (1983). Subsequently, in this study, the values for available P and K, exchangeable Ca, Mg, Al, Mn, and Na, and extractable Cu, Zn, and B were determined in the same samples using an inductively coupled plasma optical emission spectrometer (ICP - OES/Perkin-Elmer Optima 7300 DV). The analytical methodology is summarized in table 2.

The analytical values of the soil iron oxides of low (Fe_o) and high (Fe_d) crystallinity were reported by Felisberto (2009).

Semitotal metals contents

The semitotal metal contents (Cd, Co, Cr, Cu, Ni, Pb, V, and Zn) were determined by the Usepa 3050B methodology (Usepa, 1996) from 2008 to 2012 using an ICP-OES.

Table 1. Soil groups with their parent materials, distribution in the state of Rio Grande do Sul (Brazil), and the number of samples used in this study

Soil groups[1]	Parent materials	Distribution		No. of samples[3]
		Region of the state	Age of formation[2]	
1	Basalt (volcanic)	Plateau	140-130	108
2	Crystalline (granite, schist)	Southern Shield	>299	32
3	Pelitic (siltstones, mudstones)	Peripheral Depression	299-145	39
4	Sandstone (Botucatu formation)	Central Plains	145-66	51
5	Sediment (unconsolidated)	Coastal Plains	<1.8	24

[1] According to Holz (1999), Streck et al. (2008), and Fepam (2014). [2] In million years. [3] Considering the area of the state of Rio Grande do Sul (283,480 km^2); each sample represents 1,112 km^2.

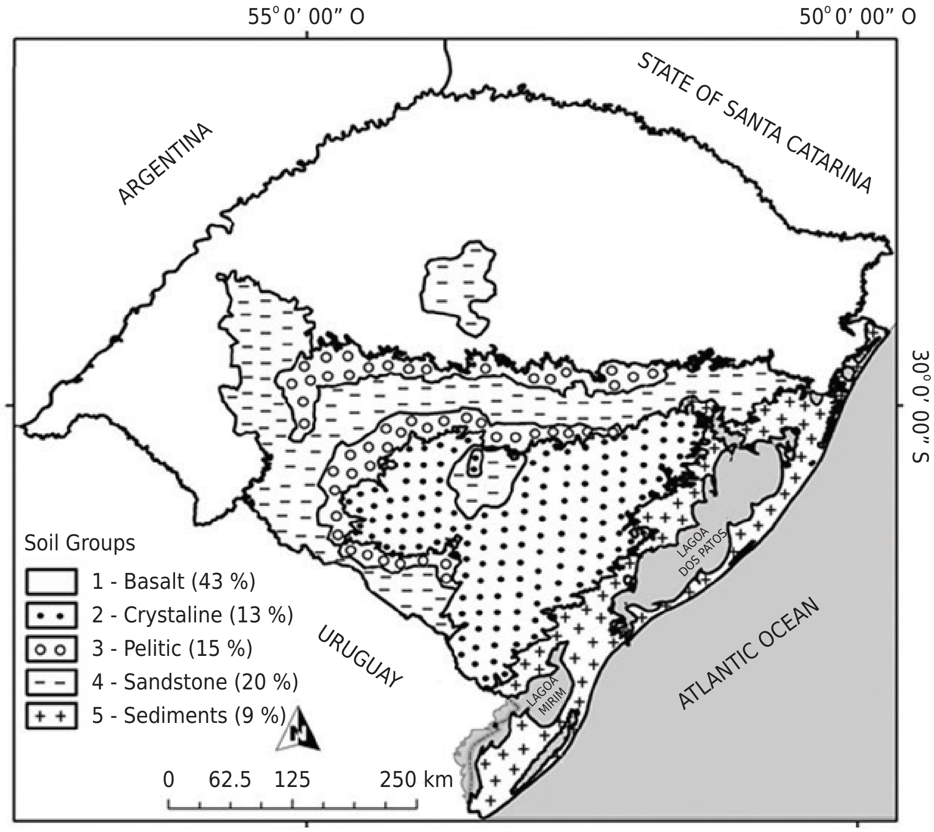

Figure 1. Map of soil groups of the state of Rio Grande do Sul (Brazil) according to soil parent material, based on the geological map (CPRM, 2006) and on the geomorphological province map (Streck et al., 2008). Source: Adapted from Fepam (2014).

Table 2. Chemical, physical, and mineralogical properties of the soil determined in the soil groups according to table 1 and analytical methodology used

Property[(1)]	Extractant (method)
pH(H_2O)	soil:water ratio of 1:1 v/v
Total acidity (H+Al)[(2)]	SMP index
Available P	Mehlich-1 method
Available K	Mehlich-1 method
Exchangeable Na	Mehlich-1 method
Exchangeable Ca	1 mol L^{-1} KCl
Exchangeable Mg	1 mol L^{-1} KCl
Exchangeable Al	1 mol L^{-1} KCl
Exchangeable Mn	1 mol L^{-1} KCl
CEC	Ca + Mg + K + Na + (H+Al)
Base saturation of the CEC (V)	(Ca + Mg + K + Na) × 100/CEC
Extractable Cu	0.1 mol L^{-1} HCl
Extractable Zn	0.1 mol L^{-1} HCl
Extractable S	$Ca(H_2PO_4)$ (500 mg L^{-1} P)
Extractable B	Hot water
Iron oxides of low crystallinity (Fe_o)	NH_4 oxalate (pH 3.0)
Iron oxides of high crystallinity (Fe_d)	Citrate/dithionite - bicarbonate[(3)]
Organic carbon	$K_2Cr_2O_7$ (Walkley and Black, 1934)
Semitotal metal[(4)]	3050B (Usepa)
Hg[(5)]	7471 (Usepa)
Particle size	NaOH dispersion (densimeter)

[(1)] According to the procedures described by Tedesco et al. (1995) or otherwise referred to. [(2)] Calculated by the equation: $(H+Al) = [e^{(10.665 - 1.1483 \times SMP)}]/10$ (SBCS/NRS, 2004, 2016). [(3)] According to the Mehra and Jackson (1960) methodology, adapted by Inda Junior and Kampf (2003). [(4)] According to the Usepa 3050B method (Usepa, 1996) (for Cd, Co, Cr, Cu, Ni, Pb, V, and Zn). [(5)] Adapted from the Usepa 7471 method (Usepa, 1998) by Felisberto (2009).

Mercury was also determined in 146 samples (selected from the 254) extracted by an HNO_3 + H_2SO_4 + $KMnO_4$ solution at 110 °C [adapted from the Usepa 7471 methodology (Usepa, 1998) by Felisberto (2009)] with cold vapor - atomic absorption spectrometry (CV-AAS).

Analytical quality control for Cd, Co, Cr, Cu, Ni, Pb, V, and Zn was verified by alternating determination of contents with use of the certified reference material BCR-142 R (IRMM, 2007) and a control soil sample from the Soil Testing Lab/UFRGS. The results from the certified material were presented by Althaus (2017). For Hg, analytical quality control is presented by Felisberto (2009).

Statistical analysis of the data for soil agricultural use

The results were statistically analyzed in the soil groups by average values. The soil properties used for lime and fertilizer recommendations for the crops were classified according to their reference value in the plant cultivation practice (CQFS-RS/SC, 2004, 2016).

Spearman correlation coefficients (r_s) were used to compare the soil properties. Statistical significance of the correlation coefficients was calculated for the 5 % probability level ($p<0.05$). The Paleontological Statistics software (PAST), version 2.6 (Hammer et al., 2001), was used.

Statistical analyses of the semitotal soil metals contents

In the data matrix, all the sample units in five soil groups were used for each of the variables (metals and soil properties).

Metals content values were studied by multivariate analysis techniques for non-parametric data through ordination analysis of the principal component analysis (PCA) type. The purpose of this was to obtain exploratory analysis to validate pattern similarity among sampling units and the distribution of the nine metals (Cd, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn) in the five soil groups according to their parent material. Analysis of variance was also conducted using a randomization test (with 1000 bootstrap interactions), comparing groups of sampling units with contrasts by the sum of the squares at a significance level of 5 % probability ($p<0.05$) from similarity measure of the Euclidean distance type in order to perform confirmatory analysis of the metal grouping.

Spearman correlation coefficients (r_s) for non-parametric data were used to compare the metals (dependent variables) with soil properties (independent variables). The statistical significance of the correlation coefficients was calculated at the 5 % probability level ($p<0.05$).

Statistical analyses were performed using the statistical programs Paleontological Statistics (PAST), version 6.3 (Hammer et al., 2001) and Multiv, version 3.31b (Pillar, 1997).

Quality reference values (QRVs) for semitotal metal analytical data

The quality reference value for the semitotal metal soil contents (Cd, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn) were calculated at the 75th and 90th percentile frequency distribution of the analytical data, according to the guidelines presented by the 420/2009 Conama Resolution (Conama, 2009) for the five soil groups. For this calculation, the values considered as "outliers" were not included (approximately 2.5 % of the samples analyzed). Outliers were considered to be the samples which had values lower or higher than the group averages plus or minus twice the standard deviation. The software Microsoft Excel was used for this computation.

RESULTS AND DISCUSSION

Soil fertility evaluation

The soil properties used for liming and macronutrient (NPK) fertilization of agricultural crops are shown in table 3. Since the average pH in all soil groups is low (<5.0), they also have exchangeable Al (8 to 20 $mmol_c\ dm^{-3}$), which can be toxic to the plants. Therefore, liming is required to increase the soil pH level to 5.5 in order to neutralize Al toxicity. For legume cultivation, however, soil pH must be raised to at least the 6.0 level, neutralizing total acidity even more.

The amounts of lime required can be established considering the crop, total soil acidity (H+Al), clay content, cation exchange capacity, and soil and crop management practices, according to current agronomic recommendations (CQFS-RS/SC, 2004, 2016).

Liming also increases the soil Ca and Mg contents, which are low in sandy soils (soil group 4). Liming can also decrease the exchangeable Mn contents, which can reach toxic levels for legumes in some soils of group 1.

Available P is the most limiting plant nutrient for agricultural crops, which was recognized as well in the first soil survey in state of Rio Grande do Sul conducted by Lemos et al. (1973). Low P soil availability and high crystallinity iron oxides (Figure 2) are found mainly in clayey soils. The P fertilization recommended for agronomic practices is based on soil clay content, plant requirements, and soil management practices (CQFS-RS/SC, 2016).

The K available to plants in uncultivated soils can be considered adequate (Table 3). As a cation (K^+) in the soil solution, its availability to plants is related to the soil cation exchange capacity (CEC). Plant potassium needs are high, and generally K must be supplied by fertilization. For that reason, not only plant requirements, but also the CEC must be considered (CQFS-RS/SC, 2016).

Soil group 1, developed over basalt, also had higher organic carbon contents (organic matter), which can be an important nitrogen source for plants. Non-legume crops generally require N fertilization.

Soils of all the soil groups showed high average levels of S and plant micronutrients (Zn, Cu, and B) (Figure 2).

Table 3. Average contents, for soil groups, of soil properties used for liming and NPK fertilization recommendations for agricultural crops

Properties[(1)]	Soil group[(2)]				
	1	2	3	4	5
pH(H_2O)	4.9	4.8	4.8	4.8	4.9
Clay (g dm^{-3})	476 (2)[(3)]	245 (3)	266 (3)	201 (4)	224 (3)
Sand (g dm^{-3})	230	583	473	693	559
Al^{3+} ($mmol_c\ dm^{-3}$)	20	10	10	8	10
P[(4)] (mg dm^{-3})	8.8	10.8	12.1	9.1	13.2
K[(5)] (mg dm^{-3})	144	137	126	84	58
Organic carbon (g kg^{-1})	38 H[(6)]	17 M	17 M	10 L	20 M
H+Al ($mmol_c\ dm^{-3}$)	119	51	66	37	52
CEC ($mmol_c\ dm^{-3}$)	198 H[(7)]	102 M	153 H	64 L	102 M

(1) Analytical methodology used according to table 2. (2) Soil groups according to table 1. (3) Textural class according to clay content in % (1: >60; 2: 41-60; 3: 21-40; 4: ≤20) (SBCS/NRS, 2004, 2016). (4) Fertilization according to the soil texture class, crop response groups, and soil management system (SBCS/NRS, 2016). (5) Fertilization according to the crop response groups and cation exchange capacity (CEC) (SBCS/NRS, 2016). (6) Organic carbon according to organic matter in % (low: ≤2.5; medium: 2.6-5.0; high: >5.0 (SBCS/NRS, 2004, 2016). (7) CEC according to the SBCS/NRS (2016) in $mmol_c\ dm^{-3}$ (low: ≤75; medium: 76-150; high: 151-300; very high: >300).

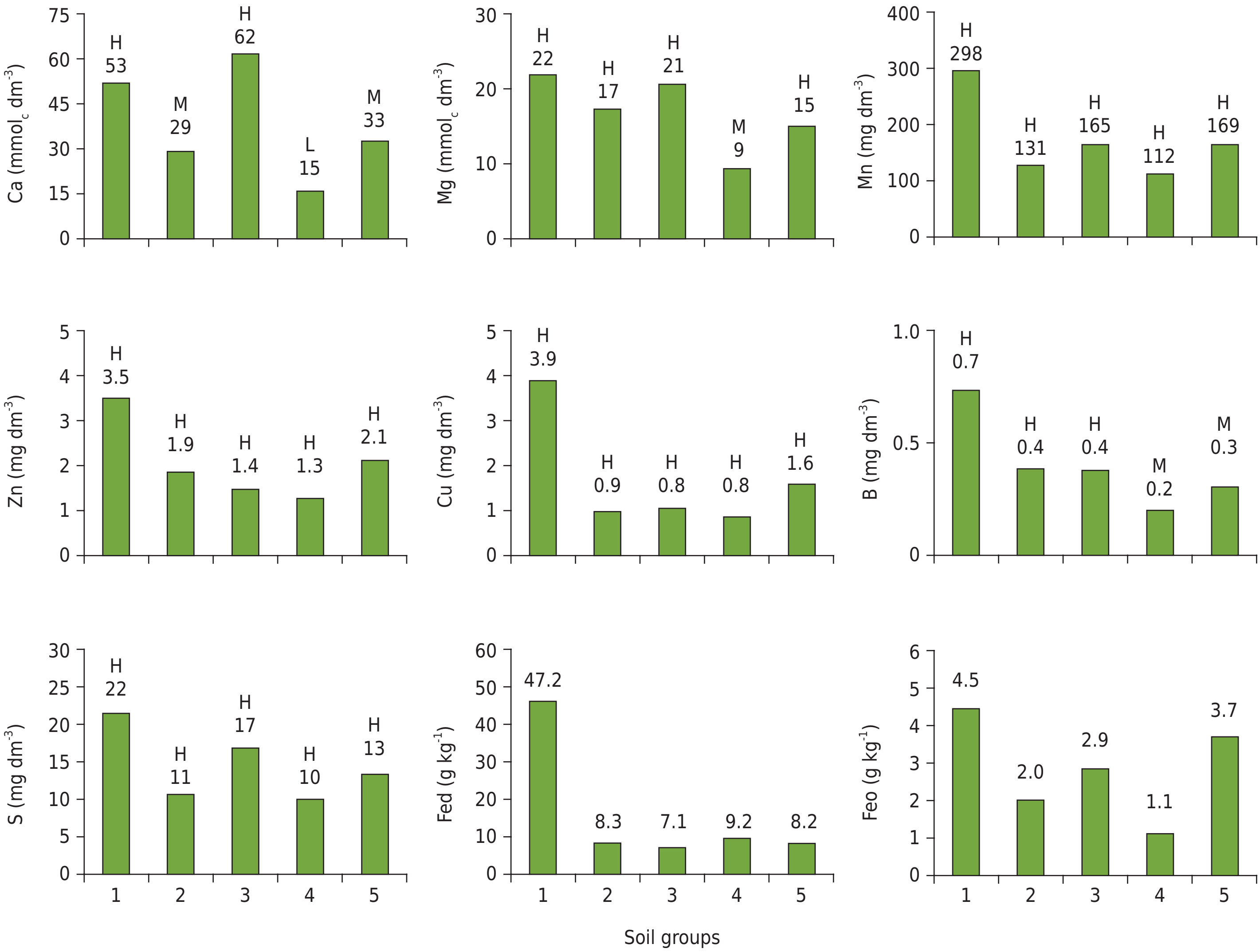

Figure 2. Average contents of exchangeable Ca, Mg, and Mn; extractable Zn, Cu, B, and S; and Fe oxides of high (Fe_d) and low (Fe_o) crystallinity in the soil groups according to table 1. L = low; M = medium; H = high, according to the SBCS/NRS (2004, 2016). Analytical methodology used according to table 2.

Semitotal metals contents

The averages and the standard deviation values obtained for the semitotal contents of the metals in the soils of the five soil groups are shown in figure 3. For the metals Cd, Co, Cr, Cu, Ni, Pb, V, and Zn, the highest average values were determined in soil group 1 (developed over basalt). The highest average value was found for V (278 mg kg^{-1}) and the lowest for Cd (0.41 mg kg^{-1}). The average values in the other soil groups decreased in the order: Cu > Zn > Cr > Co > Pb > Ni.

Mercury, however, showed a different trend - the semitotal values are much lower than those for the other metals (an average of 0.05 mg kg^{-1} for soil group 1). But the average value for soil group 5 was similar to this. This is probably due to some anthropic influence, since the samples were taken from recent sedimentary deposits.

For statistical study of the data, principal component analysis (PCA) was used, with analysis of variance by randomization tests and Spearman correlation between metals contents and soil properties.

Based on statistical analysis, quality reference values (QRVs) for the soils of the state of Rio Grande do Sul were suggested and compared with others adopted by several Brazilian states/regions and by the Conama.

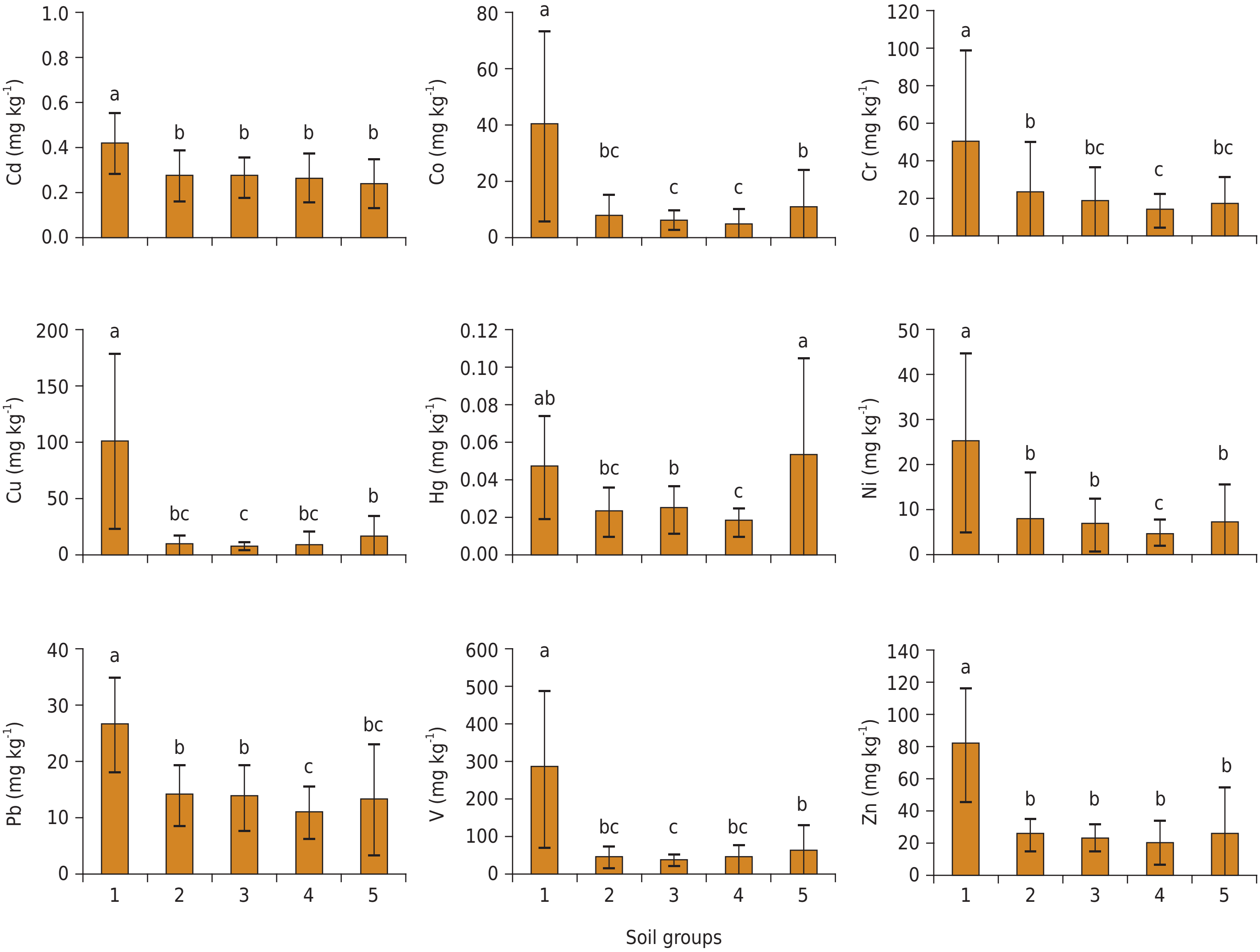

Figure 3. Average contents of semitotal Cd, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn in the soil groups according to table 1. Averages with the same letters are not statistically different in the randomization test from Euclidean distance ($p<0.05$). Vertical bars indicate the standard deviation.

Principal component analysis

The ordination diagram obtained by PCA (Figure 4) synthesizes the metals values in their soil groups for all sample units distributed along ordination axes (principal components). Multivariate techniques, such as PCA, allow inferences regarding data sets at a known level of significance and thus allow a wide range of understanding of the overall distribution of results (Paye et al., 2012).

The pattern of distribution of sample units was considered stable, since the first axis allowed explanation of 62 % of variation and axis 2 allowed 13 %.

The distribution of the sample units of the metals relative to axes 1 and 2 of the diagram is according to greater or lesser similarity among the units. For all sampling units, a greater gradient along axis 1 was observed, in which most sampling units were located on the right side of the diagram, corresponding to soil group 1, and most sampling units corresponding to the other soil groups (2 to 5), were located on the left side, which were therefore grouped together, thus showing greater similarity among units. Considering their parent materials, the sample units in soil groups 2 to 5 were previously classified in different groups, but from principal component analysis, the similarities of these groups were observed. Therefore, by the PCA, we can establish a new grouping, namely, the soil group formed over basalt (soil group 1) and the soil groups developed over the other parent materials (soil groups 2 to 5). In the study of Burak et al. (2010), the PCA method was also performed to better quantify the relationships among the variables and to identify groups of geochemically similar samples.

As for the sample units, the metals, represented by vectors in the ordination diagram (Figure 4), were also more concentrated along axis 1, with the highest percentage of explanation of the distribution of sample units, since the highest correlation coefficient for the metals (with the exception of Cd) obtained by PCA are on axis 1. Mercury, although with a higher correlation coefficient related to axis 1 than axis 2, showed low correlations for both axes (Table 4).

The proximity of the metals projected in the ordination diagram obtained by PCA analysis indicates the similarity among them. This is also shown by calculating the Spearman correlation coefficients (r_s) for these same metals (Althaus, 2017), where high positive values ($r_s \geq 0.65$; $p<0.05$) between several metals were observed. A significant and positive correlation coefficient suggests similar geochemical behavior and/or a common source material of these elements (Burak et al., 2010). Exceptions were observed for Cd and Hg, which, as represented in the PCA diagram, were at a greater distance from axis 1 and thus from the other metals and showed the lowest correlation coefficients.

The projection of the metal in the ordination diagram also indicated in which direction the metals showed an upward trend. Each one went to the right side of the diagram, the side in which the sampling units corresponding to soil group 1 are also projected (Figure 4). This indicates that the metals exhibit an upward trend of their contents in soil group 1 (soils formed over basalt), and the opposite trend is obtained for the other groups, also showing the difference between soil group 1 and soil groups 2 to 5.

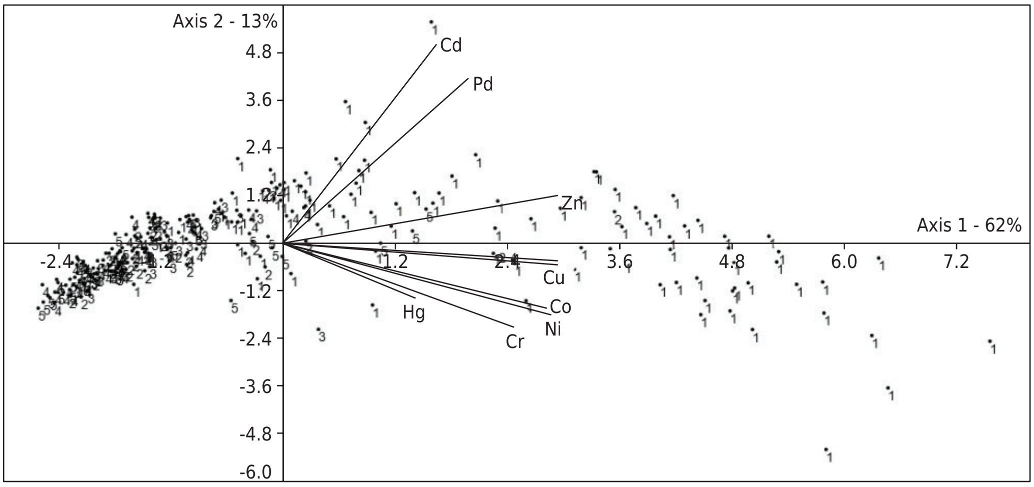

Figure 4. Ordination diagram obtained by principal component analysis for metals and soil groups, according to table 1. The metals are represented by vectors and soil groups by dots.

Table 4. Correlation coefficients obtained by principal component analysis relating metals to the axes of the ordination diagram

Metal	Axis 1	Axis 2
Cd	0.52	0.73
Co	0.89	-0.24
Cr	0.78	-0.31
Cu	0.92	-0.07
Hg	0.45	-0.20
Ni	0.91	-0.27
Pb	0.62	0.61
V	0.92	-0.08
Zn	0.92	0.18

Analysis of variance by randomization tests

The randomization test to compare soil groups for metals, using the similarity measure of the Euclidean distance type, showed the existence of contrasts by summing the squares at the significance level of 5 % probability ($p<0.05$). This corroborates conventional analysis of variance in indicating that there is a statistically significant difference between metals of soil group 1, which have the highest metals contents, and the metal values from the other soil groups, except for Hg (Figure 3).

Analysis of variance with randomization tests for multivariate data was used as confirmatory analysis of the metal grouping results already obtained by exploratory PCA analysis. Analysis of variance confirmed the difference in metals contents of soil group 1, with basalt as the main parent formation material, compared to the other groups. Soils derived from basaltic materials contain large heavy metals contents (Kabata-Pendias, 2011). As a result of these findings, not five different soil groups (Figure 3) but rather maintenance of soil group 1 and unification of soil groups 2 to 5, called soil group 2-5, were established for the metals studied, as presented in table 5.

Spearman correlation between metals and soil properties

Spearman correlation coefficients (r_s) between metals and the main soil properties are presented in table 6. The values of the correlation coefficients are important for identifying the soil properties that most influence retention of metals in soils and their distribution in the different environmental compartments.

The highest values ($r_s \geq 0.65$; $p<0.05$) for metals (except for Cd and Hg) were observed in the clay, Fe_d, and extractable Cu soil properties (Table 6). The clay fraction (and silt, to a lesser extent) contains the main mineral adsorbents in the soil, such as Fe and Al oxides, and therefore has considerable influence on the distribution of trace elements in the soil profile (Kabata-Pendias, 2011).

Another highly significant positive correlation coefficient was found between Cu or Zn and organic carbon. The same result was reported by Biondi et al. (2011). This can be explained by the fact that Cu and Zn ions have affinity with the humified organic matter fraction of the soil (Melo et al., 2008).

The pH(H_2O) showed the lower correlation values with the metals (Table 6). According to Fadigas et al. (2002), this may be due to the use of a strongly acidic solution to determine the semitotal metals contents. Significant correlations could be obtained when using diluted acidic solutions or complexing agents (Paye et al., 2012).

Table 5. Average contents, standard deviations, and ranges of semitotal Cd, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn in soil group 1 and soil group 2-5

Metal	Soil group 1[1]		Soil group 2-5[1]	
	Average and standard deviation	Range	Average and standard deviation	Range
	mg kg^{-1}			
Cd	0.41±0.14 a[2]	0.07-0.81	0.26±0.11 b	0.06-0.63
Co	39±34 a	4-173	7±8 b	1-45
Cr	50±49 a	8-308	17±19 b	2-163
Cu	100±78 a	8-309	10±12 b	0.5-68
Hg	0.05±0.03 a	<0.03-0.12	<0.03±<0.03 a	<0.03-0.13
Ni	25±20 a	3-103	6±7 b	1-61
Pb	26±9 a	9-71	13±6 b	2-38
V	278±212 a	36-794	42±40 b	1-195
Zn	81±36 a	10-222	23±16 b	2-106

[1] Soil groups according to table 1. [2] Averages followed by the same letters in the lines are not statistically different in the randomization test from the Euclidean distance ($p<0.05$).

The complete list of the Spearman correlation coefficients (r_s) between the soil properties is presented by Althaus (2017).

Quality reference values (QRVs)

According to Conama Resolution 420/2009, the soil QRVs can be established considering the 75th or 90th percentiles (Conama, 2009). These values are presented by Althaus (2017) for the five soil groups of RS, as already mentioned (Althaus et al., 2014), for the metals Cd, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn in soils. These values were adopted, with some adaptions, by the 85/2014 Fepam Ordinance (Fepam, 2014).

Considering the large areas of the groups and the geomorphological and pedogenetic diversities in every state, and even more so in the country, the establishment of soil QRVs for smaller areas is justified, with technical and statistical support. Furthermore, each soil residues disposal project should include “blank” areas for reference as the operations proceed and for the decision-making to occur safely.

The QRVs for native metals contents in the soils of RS at the 90th percentile are presented in two categories (Table 7): one for soils developed over basalt and the other as the averages of the remaining soils (soil groups 2 to 5, table 1).

Table 6. Spearman correlation coefficients (r_s) between soil properties and metals. Correlation coefficients >0.65 are in bold

Soil property	Metal								
	Cd	Co	Cr	Cu	Hg	Ni	Pb	V	Zn
Clay	0.57*	**0.75***	**0.70***	**0.84***	0.44*	**0.75***	**0.82***	**0.82***	**0.84***
pH(H_2O)	0.00	0.28*	0.25*	0.15*	0.15	0.26*	0.00	0.16*	0.17*
H+Al	0.33*	0.24*	0.21*	0.37*	0.21*	0.27*	0.47*	0.33*	0.36*
Exchangeable Ca	0.22*	0.53*	0.51*	0.41*	0.32*	0.56*	0.30*	0.40*	0.46*
Exchangeable Mg	0.32*	0.62*	0.62*	0.53*	0.34*	**0.69***	0.40*	0.52*	0.59*
CEC	0.43*	0.59*	0.48*	0.64*	0.46*	0.60*	0.62*	0.57*	0.65*
Extractable Cu	0.45*	**0.80***	**0.69***	**0.86***	0.39*	**0.77***	**0.66***	**0.83***	**0.78***
Extractable Zn	0.24*	0.49*	0.34*	0.44*	0.46*	0.41*	0.35*	0.42*	0.51*
Exchangeable Mn	0.24*	**0.69***	0.53*	0.55*	0.26*	0.57*	0.42*	0.55*	0.54*
Fe_d	0.64*	**0.84***	**0.79***	**0.89***	0.51*	**0.81***	**0.80***	**0.92***	**0.89***
Fe_o	0.37*	**0.66***	0.52*	**0.67***	0.47*	0.61*	0.60*	0.61*	0.64*
Extractable B	0.49*	0.64*	0.58*	**0.68***	0.54*	0.63*	**0.66***	**0.66***	**0.69***
Organic carbon	0.52*	0.61*	0.45*	**0.66***	0.47*	0.58*	0.64*	0.59*	**0.67***

*: significant correlation at a significance level of 5 % ($p<0.05$).

Table 7. Average quality reference values (QRVs) for metals, in the 90th percentile, by soil groups for the natural metals contents in soils of the state of Rio Grande do Sul (Brazil)

Metal	Soil group[(1)]	
	1	2-5[(2)]
	mg kg^{-1}	
Cd	0.59	0.39 (0.36-0.42)
Co	75	14 (7-29)
Cr	94	28 (21-40)
Cu	203	17 (9-37)
Hg	0.07	0.05 (<0.03-0.10)
Ni	47	10 (7-12)
Pb	36	20 (16-27)
V	567	89 (48-177)
Zn	120	31 (29-33)

[(1)] Soil groups according to table 1. [(2)] Average for the soil groups and variation (in parentheses).

Soil mapping units, or even soil classes, were not considered in this study. Mello and Abrahão (2013) pointed out that the soil classification system criteria mainly considers soil genesis and not semitotal heavy metals contents.

Several Brazilian states, such as São Paulo (Cetesb, 2014), Minas Gerais (Copam, 2011), Mato Grosso (Santos, 2011), Rondônia, Rio Grande do Norte (Preston et al., 2014), and the Archipelago of Fernando de Noronha (Fabricio Neta, 2012), have adopted the 75th percentile, which is more restrictive. However, other states, including RS, have adopted the 90th percentile.

The 75th percentile is more restrictive to soil use, since it assumes that 25 % of the soils are "naturally contaminated" and cannot be used, even for food production. This leads to a paradoxical situation: on the one hand, agencies concerned about the environment forbid use of the soil, and, on the other hand, there is a shortage of areas for cultivation and, consequently, lower food production. For that reason, some authors (Melo Junior, 2008; Paye et al., 2010) point out that, even with use of the 90th percentile, there are at least 10 % "naturally contaminated" soils. For that reason, use of the 90th percentile is more commonly accepted by government agencies in the European Community and the USA.

In our study (a population of 254 soil samples), 2.5 % of them were excluded as outliers. With use of the 90 percentile, we would have 12.5 % of the soil "naturally contaminated", which seems very strange, to say the least.

However, if the proposal of Conama Resolution 420/2009 for prevention values (PV) and investigation values (IV) (Althaus, 2017) is accepted, more strange situations will be observed for soil group 1: (1) the QRV for Co, Cr, Cu, and Ni are higher than their prevention values (PV); (2) the QRV for Co is higher than the agricultural and residential investigation value (IV). Moreover, for soil groups 2 to 5, the maximum variation of the QRV for Co is higher than the proposed PV. It can be seen, therefore, that 43 % of the soils of RS (developed over basalt) are "naturally contaminated" by some metal or another.

The situation of the Archipelago of Fernando de Noronha, a supposedly non-contaminated environment, is at least as strange, since some QRVs for metals are higher than the Conama PV and IV values (Fabricio Neta, 2012).

In Minas Gerais, the QRV for Cr was also observed to be higher than the PV (Mello and Abrahão, 2013). This State Environmental Agency therefore decided to use the PV (proposed by the Cetesb) as the QRV.

The whole strange situation comes from Conama's decision to adopt the data obtained by the Cetesb for the whole country; the Cetesb used few soil samples with small diversity (Cetesb, 2001, 2005, 2014), similar to the parent materials of RS soil groups 3 (pelitic) and 4 (sandstones).

Therefore, we suggest that due to the large diversity of the parent materials and pedogeomorphological and pedogeoclimatic conditions, each state or region should propose and use its own QRV based on standardized sampling and an analytical methodology, as well as a suitable statistical basis.

Furthermore, the use of the QRVs as proposed by Conama Resolution 420/2009 does not consider the agricultural use of organic residues generated by food production (poultry, swine, and cattle raising) or industrial (tanneries) and urban (sewage sludge and organic compost) activities. That means that a different approach must be used for disposal of such residues in the soil, a practice highly recommended for several thousands of years in organic agriculture. The interactions between soil properties, residue composition, plant uptake, and effects of metals on living beings (animal and human) must be considered, as suggested earlier (Quadro, 2008; Giasson and Tedesco, 2010).

CONCLUSIONS

Average values of available P contents are low in all soil groups, but are high in several soil groups for available K. Averages of total acidity and cation exchange capacity are higher in the soils developed over basalt (soil group 1). The average values of extractable Zn, Cu, and S are high in all soils. Averages of Fe oxides are higher in the soils formed over basalt than in the other soils.

Average metal (Cd, Co, Cr, Cu, Ni, Pb, V, and Zn) contents were higher in Group 1 soils than in the other soil groups (2 to 5). For Hg, however, average values are similar for all soil groups.

The Spearman correlation coefficients are positive and highest between the metals (except for Cd and Hg) and the clay, Fe_d, and extractable Cu soil properties. Another high positive correlation coefficient was found between semitotal Cu and Zn contents and organic carbon.

The quality reference values (QRVs) for Cd, Co, Cr, Cu, Hg, Ni, Pb, V, and Zn, determined according to the National Commission for the Environment (Conama Resolution 420/2009), followed the same trend as the average metals contents.

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