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Reference Values of Soil Quality for the Rio Doce Basin

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ABSTRACT: The great geological and soil variation in the state of Minas Gerais, Brazil, indicates the need for regional studies to understand the geochemical background of soils. The Rio Doce Basin became a priority area for geochemical background determination after the rupture of the tailings dam of Fundão in 2015. In this context, the objectives of this study were to propose Reference Values of Soil Quality in the Rio Doce Basin, to define variables that can predict metal(loid) concentrations in the soil, and to examine the correlation between metal(loid) concentrations determined by X-ray fluorescence and by the traditional method. One hundred and seven samples were collected from minimally disturbed areas, representing the main soils and source materials. Metal(loid)s were determined by acid digestion and X-ray fluorescence. Descriptive statistics of the data, as well as the calculation of the Randomized Dependence Coefficient (RDC) and Principal Component Analysis (PCA) were carried out. The soils were found to be acidic, dystrophic with low Mehlich-1 extracted P contents, and have a variable texture. The coefficient of determination ranged from 0.4 to 0.9, suggesting X-ray fluorescence as a promising technique for determining metal(loid) concentrations in soils. The absence of correlation between clay and organic matter contents with metal(loid) concentrations suggests that the latter were inherited exclusively from the parent material, with little influence of pedogenesis. Metal mineralization in the highlands that constitute the topographic drainage divide of the basin increase the reference values of soil quality to higher values than established for the State of Minas Gerais.

Keywords: RDC, Iron Quadrangle, heavy metals, soil quality reference values, Mariana.

INTRODUCTION

The Rio Doce is one of the most important watercourses in the Brazilian Southeast region, supplying more than 20 municipalities in the states of Minas Gerais and Espírito Santo. Mantiqueira and Itacolomi highlands are the topographic drainage divides of the Rio Doce Basin (RDB), and home to a biodiversity hotspot of the planet (Puig, 2001).

Due to its mineral resources, the RDB was important for the colonization of the Brazilian southeast. Gold and diamond exploration peaked in the second half of the eighteenth century, with manual gold washing. In addition, Al, Au, Cr, Fe, Mn, Ni, Sb, marble, quartzite, sand, and precious stones are exploited in the RDB (Dardenne and Schobbenhaus, 2001; DNPM, 2017).

One of the largest environmental disasters ever recorded in Brazil occurred in November 5, 2015, when an iron ore tailings dam broke in the municipality of Mariana, state of Minas Gerais. Between 40-65 million m³ of water and sediment flowed 700 km downstream, from the rupture point to the Rio Doce estuary. More than 30 deaths were reported among mining workers and village residents near the dam. Aside from affecting animal and plant life in the river and on its banks, the transported mud obstructed the public water supply of approximately one million people for a week, affecting indigenous tribes and 40 cities of the two Brazilian states bathed by the Rio Doce (Meira et al., 2016). Several private and public projects are being funded to recover the ecosystem of one of the most important basins in Brazil. However, little is known about the real environmental impact caused by the mud (Lambertz and Dergan, 2015; Massante, 2015).

For the identification of contaminated areas, a single Soil Quality Reference Value (QRV) per potentially toxic chemical element was established in 2011, for the entire state of Minas Gerais (Copam, 2011). The QRV is calculated statistically, represented by the upper quartile of a database after removal of the outliers (Conama, 2009; Fernandes et al., 2015). However, these outliers may represent anomalous areas and require specific reference values. Studies indicated which only one QRV for the entire State of Minas Gerais does not represent the geochemical diversity of the soils (Souza et al., 2015). In this case, regionalized reference values would ensure successful monitoring. The law that defines the criteria and guidelines of soil quality values (Conama, 2009) allows regionalized QRV in the Brazilian states, as already applied in the state of Rio Grande do Sul (Fepam, 2014) and underway for other biomes (Coringa et al., 2014).

Despite the importance of the RDB for the water supply of the population in the Southeastern region, the soils in the Rio Doce Basin are little studied, mainly in the region of the river source and the areas of the Iron Quadrangle (Costa, 2003; Reis et al., 2014). Therefore, further studies are needed, mainly to determine the natural metal(loid) concentrations. These studies can help to interpret the behavior of chemical elements in tropical soils and especially guide environmental intervention measures.

For the metal(loid) determination in soils, Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is frequently used, due to its low detection limit and cost in relation to other techniques. The X-ray fluorescence method stands out for a faster metal(loid)s determination, without costs for reagents and waste resulting thereof. Unfortunately, the method has no detection limits comparable to ICP-OES for most elements, but can serve as a rapid screening tool for contaminated soils (Towett et al., 2013; McComb et al., 2014). Thus, the objective of this study was to analyze the variability of metal(loid) concentrations in soils of the Rio Doce Basin. In addition, correlations between the metal(loid) concentrations in soils detected by X-ray fluorescence and with the traditional method were investigated, and Quality Reference Values for soils in the Rio Doce Basin were established.

MATERIALS AND METHODS

Study area

The RDB has a total area of approximately 84,000 km², of which 14 % lie in the state of Espírito Santo and 86 % in Minas Gerais. The study area covers a portion of the RDB in the territory of Minas Gerais, corresponding to the upper and the middle portions of the Basin (Figure 1).

The climate is tropical humid with average precipitation close to 1,500 mm and mean temperature between 18 and 24 °C (Nunes et al., 2009). The regional relief is classified as hilly and mountainous, with hills and valleys formed by the dissection of old surfaces and cliffs, where more resistant rocks stand out or raised in a Proterozoic horst-graben system, reactivated during the Cretaceous and Cenozoic (Vieira and Gramani, 2015). Archaean and Paleoproterozoic banded iron-formations and quartzites constitute the highest areas in the west and north of the basin, while in the south, Neoproterozoic granitoids, granites and gneisses in horsts form the southern drainage divides (Figure 1).

Spatial soil distribution is closely associated with relief and geology (Table 1). Ferralsols (*Latossolos* – Brazilian System of Soil Classification) and Acrisols (*Argissolos*) represent 86 % of the total area, in a scenario of deeply weathered soils. Haplic Cambisols (*Cambissolos*), Haplic Leptosols (*Neossolos Litólicos*), Haplic Regosols (*Neossolos*
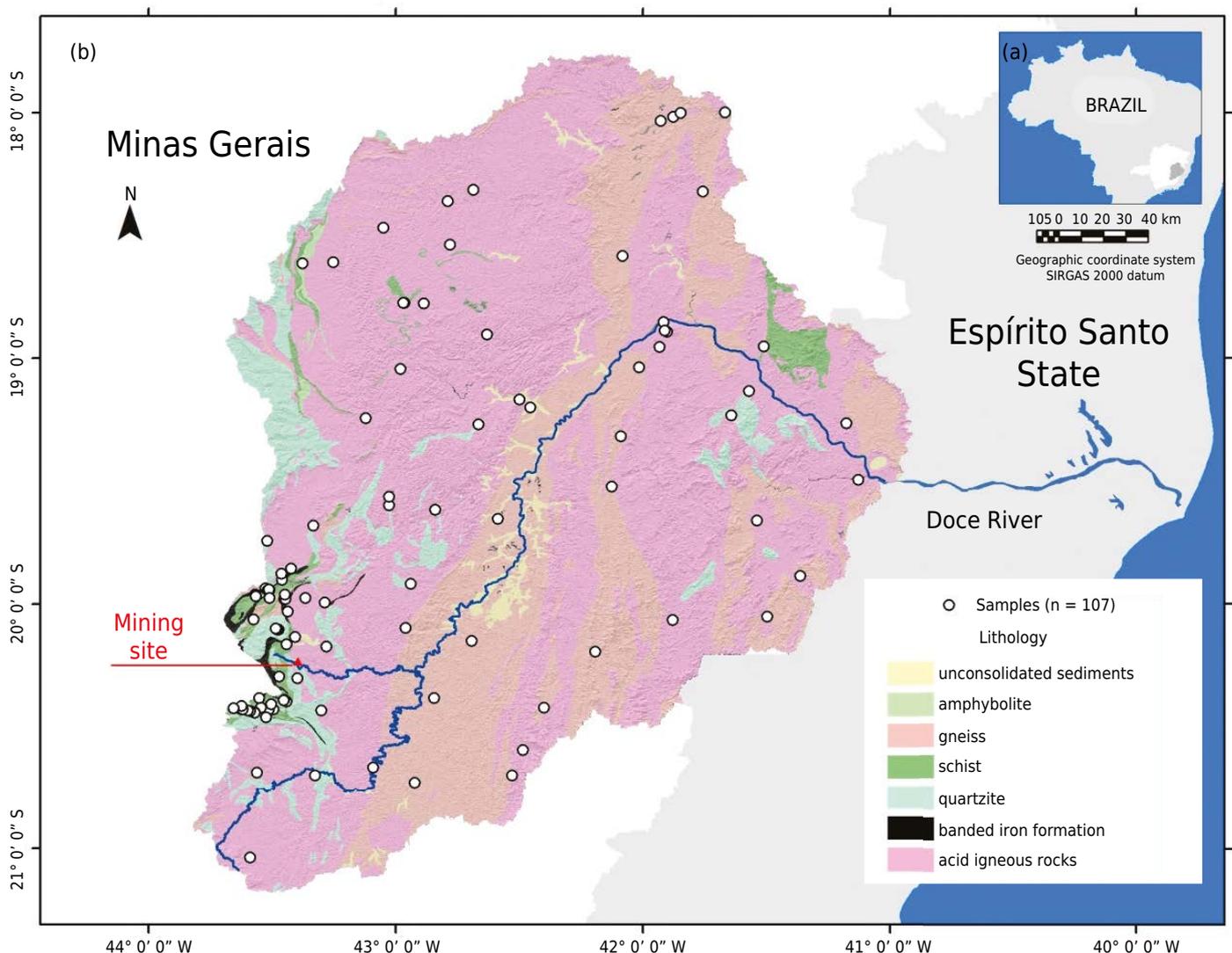
Figure 1. Location of Minas Gerais state (a) and samples collected in study area according to the lithology (b).

Regolíticos), and rock outcrops are found at 1,000 m above sea level. These soils occur in ridges and structural scarps, associated to Archean quartzite, Neoproterozoic banded iron-formation, quartzite and schist, or geological faults. "Red" Haplic Ferralsols (between 700 and 850 m a.s.l.), "Red-Yellow" Haplic Ferralsols (between 500 and 850 m a.s.l.) and "Yellow" Haplic Ferralsols (between 500 and 800 m a.s.l.) are found in association with saprophyte of Paleoproterozoic gneiss and granite at the top of residual hills. Haplic Nitosols (*Nitossolos Háplicos*) and "Red" Haplic Acrisols occur between 350 and 500 m a.s.l., associated to metaultrafic rocks and granodiorites, in the lower slopes. "Red-Yellow" Haplic Acrisols (between 350 and 500 m a.s.l.) are observed on paleogenic fluvial terraces. Gleysols (*Gleissolos*) and Fluvisols (*Neossolos Flúvicos*) (between 250 and 350 m a.s.l.) developed from unconsolidated sediments in alluvial plains of the Rio Doce (Nunes et al., 2001; CPRM, 2003; Universidade Federal de Viçosa/Fundação Centro Tecnológico de Minas Gerais/Universidade Federal de Lavras/Fundação Estadual do Meio Ambiente, 2010).

Approximately 98 % of the basin area belongs to the Atlantic Forest biome, composed of dense and mixed tropical rain forests, seasonal semideciduous and deciduous forests, mangroves, and resting vegetation. It is estimated that the biome hosts about 250 species of mammals (55 endemic), 340 amphibians (90 endemic), 1,023 birds (188 endemic), and about 15,000 species of trees (7,432 endemic), 843 ferns (834 endemic), and 1,337 bryophytes (242 endemic) (Puig, 2001; BFG, 2015; Costa and Peralta, 2015; Prado et al., 2015). Regardless of its importance, the Atlantic Forest is the most threatened biome in Brazil; only 7.9 % of the original area exists in forest remnants in fragments above 100 ha, representative for the conservation of biodiversity. Minas Gerais is the state with the largest deforested area of the biome. Approximately 2.8 % of the remnants are still primary forest, which occur mainly as isolated and dispersed fragments in a landscape dominated by agriculture and livestock (Fundação SOS Mata Atlântica/Instituto Nacional de Pesquisas Espaciais, 2015).

Table 1. Soil occurrence in the study area

Soil Group[1]		Lithology[4]	Area
WRB[2]	SiBCS[3]		%
"Red" Haplic Acrisols (ha AC 'a')	*Argissolos Vermelhos Distróficos*	Granite and granitoid	17.0
"Red-Yellow" Haplic Acrisols (ha AC 'b')	*Argissolos Vermelho-Amarelos Distróficos*	Gneiss	6.2
Haplic Cambisol (ha CM)	*Cambissolos Háplicos Distróficos*	Banded iron-formation, quartzite, schist, gneiss, granite, granitoid and mafic rocks	5.5
Haplic Gleysol Humic (ha GL hu)	*Gleissolos Háplicos Tb Distróficos*	Unconsolidated sediments	<0.1
"Yellow" Haplic Ferralsol (ha FR 'a')	*Latossolos Amarelos Distróficos*	Gneiss	2.3
"Red" Haplic Ferralsol (ha FR 'b')	*Latossolos Vermelhos Distróficos*	Banded iron-formation, mafic rocks and granitoid	15.5
"Red-Yellow" Haplic Ferralsol (ha FR 'c')	*Latossolos Vermelho-Amarelos Distróficos*	Gneiss, granite and granitoid	48.1
Haplic Fluvisols (ha FL)	*Neossolos Flúvicos Tb Distróficos*	Unconsolidated sediments	0.5
Haplic Leptsols (ha LP)	*Neossolos Litólicos Distróficos*	Banded iron-formation, quartzite, schist, gneiss and phyllite	3.2
Haplic Nitisols (ha NT)	*NitossoloS Háplicos Distróficos*	Mafic rocks and granodiorite	<0.1
Haplic Regosols (ha RG)	*Neossolos Regolíticos Distróficos*	Gneiss	0.4
Rock outcroup	*Afloramentos rochosos*	Quartzite and banded iron-formation	1.2

[1] Universidade Federal de Viçosa/Fundação Centro Tecnológico de Minas Gerais/Universidade Federal de Lavras/Fundação Estadual do Meio Ambiente, (2010). [2] IUSS Working Group WRB (2014). [3] Santos et al. (2013). [4] CPRM (2003).

Sample preparation and metal(loid) analysis

Soils samples collected before the disaster in 2012 were provided by the Soil Bank Database of Minas Gerais State. The topsoil layer (0.00-0.20 m) was collected according to procedures established by Abrahão and Marques (2013). Stainless steel equipment was utilized to sample a total of 107 sites (Figure 1). Sampling was avoided in areas close to potential sources of contaminants.

The samples were air-dried and sieved (2 mm). The physical and chemical properties of the samples were determined according to procedures proposed by Claessen (1997). Sand, silt, and clay contents were determined by the sieve-pipette method. Soil pH was measured in a 1:2.5 soil:water solution. Exchangeable Ca, Mg, and Al contents were determined in 1 mol L^{-1} KCl solution, while K^+ and Na^+ were determined in Mehlich-1 solution. Potential acidity (H+Al) was determined by titration in ammonium acetate buffered to pH 7.0. Cation exchange capacity (CEC) was calculated based on the above data. Soil organic matter (SOM) was determined by the oxidation of organic matter with potassium dichromate in sulfuric medium, correcting the content by a conversion factor of 1.724. The P adsorption capacity was determined after agitation of 2.5 g soil in $CaCl_2$ 0.01 mol L^{-1} solution containing 60 mg L^{-1} P for 1 h. The solution was filtered and remaining P (P-rem) determined by photocolorimetry.

The samples were ground and sieved through a 200 mesh stainless steel sieve. An aliquot of these samples was solubilized by acid digestion according to the SW-846 EPA method 3051A (Usepa, 2007). The Al, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sr, V, and Zn contents were determined by ICP-OES, using a Perkin Elmer model Optima DV 7300. Arsenic, Se, Sb, and Hg were determined with a hydride generator coupled to ICP-OES. The standard reference materials Montana Soil I and II were digested and the same analytes were determined as described above. The recovery rate calculated for each metal and metalloid varied between 80 and 120 %, which is considered satisfactory (Table 2).

Table 2. Reference material analyses expressed as percentage of nominal analyses

Element	Montana I Soil (n =15)	Montana II Soil (n =15)
	%	
Al	111.15	113.87
Ag	85.41	86.71
As	106.90	114.04
B	-[1]	-
Ba	90.75	100.22
Cd	132.81	104.87
Co	100.59	105.57
Cr	100.15	97.15
Cu	102.45	97.80
Fe	99.66	113.64
Hg	112.58	105.80
Mn	89.00	118.50
Mo	-	-
Ni	95.91	84.19
Pb	104.56	109.65
Sb	102.46	107.51
Se	101.79	97.95
Sr	-	-
V	102.55	103.14
Zn	101.09	112.60

[1] No certified values are available for Bo, Mo, and Sr.

Arsenic, Al, Ca, Co, Cr, Cu, Fe, K, Hg, Mg, Mn, Na, Ni, Pb, Sb, V, and Zn contents were also determined by X-ray fluorescence spectrometry with pressed powder pellets. The samples were sieved (200 mesh) and pressed in a hydraulic press (4 t cm^{-2} for 1 min), to a mass per unit area of 300 mg cm^{-2} (Alves et al., 2015a) for sandy soil samples, two drops of polyethylene glycol solution (PEG 100-6,000 g L^{-1}) were added as binder material. The chemical elements were quantified by the Fundamental Parameter method (Quantitative - FP). Calibration consisted of adjusting the sensitivity coefficients of each element analyzed. The sensitivity coefficients of the Quantitative were achieved by FP method, based on four reference samples: Montana Soil II - NIST 2711a, BHVO - 2 - Basalt - USGS, COQ - 1 - Carbonatite - USGS, and SDC - 1 - Mica Schist - USGS (Alves et al., 2015b).

Statistical analysis

Descriptive statistics were calculated for all 107 samples as well as for each soil group. In case of non-normal data distribution, the Randomized Dependence Coefficient (RDC) was calculated between variables of soil properties and categorical variables with metal(loid) contents. The RDC determines dimensionless non-linear relationships among the original data by computing the highest canonical correlation between nonlinear projections of their respective copula transformations (Lopez-Paz et al., 2013).

The following categorical variables were used: a) digital elevation model based on SRTM images (courtesy of USGS), using altitude and slope; b) soil use and vegetation cover (Jun et al., 2014); c) gamma-spectrometry (CPRM, 2003); d) climate data (Hijmans et al., 2005), such as d.1) annual mean temperature; d.2) mean diurnal range; d.3) isothermality; d.4) temperature seasonality (coefficient of variation × 100); d.5) maximum temperature of warmest month; d.6) minimum temperature of coldest month; d.7) annual temperature range; d.8) mean temperature of wettest month; d.9) mean temperature of driest month; d.10) mean temperature of warmest month; d.11) mean temperature of coldest month; d.12) annual precipitation; d.13) precipitation of wettest month; d.14) precipitation of driest month; d.15) precipitation seasonality (coefficient of variation); d.16) precipitation of the wettest quarter; d.17) precipitation of driest quarter; d.18) precipitation of warmest quarter; d.19) precipitation of coldest quarter; and e) lithology (Pedrosa-Soares et al., 1994).

Principal Component Analysis (PCA) was performed to clarify the relationship between the variables. This multivariate technique transforms correlated variables into uncorrelated variables, called principal components (PCs). The PCs are ordered by decreasing their eigenvalues that express the data variability. Consequently, considering only the higher own-value PCs, the number of variables reduce without losing the descriptive power. Prior to PCA, analytical data were transformed logarithm and standardized to provide a normal distribution.

Soil QRVs for each metal(loid) were calculated using the 75 % percentile by the box-and-whisker plot method (Conama, 2013). Outliers were excluded, considering an upper limit of 15 % of the sample.

RESULTS

The soil surface of the RDB is generally acidic, with low P availability (P_M) and low CEC (Table 3). In approximately 75 % of the samples, the SOM exceeded 2.5 %. The coefficients of variation were highest for the contents of Ca^{2+}, Mg^{2+}, Al^{3+}, and base saturation (V%). The soils were characterized as clayey (Ferralsols, Nitisols, Acrisols, and Fluvisols), loamy (Cambisols, Leptosol, and Regosols), and sandy (Gleysols) (Table 3).

Leptosols and Regosols have the highest coefficients of variation for pH(H$_2$O), sum of bases (SB), CEC, SOM, and texture. The lowest coefficients of variation were recorded

Table 3. Descriptive statistics (median - coefficient of variation %) of topsoil properties for soil groups and literature data

Soil[1]	pH(H₂O)	P_M	K⁺	Ca²⁺	Mg²⁺	Al³⁺	H+Al	SB	CEC	V%	SOM	P_Rem	Sand	Silte	Clay	Fe	Al
		⎯ mg kg⁻¹ ⎯		⎯⎯⎯ cmol_c kg⁻¹ ⎯⎯⎯						%	dag kg⁻¹	mg L⁻¹	⎯ g kg⁻¹ ⎯			⎯ dag kg⁻¹ ⎯	
ha AC 'a' (3)	5.7-13	1.6-87	80-57	2.8-60	0.8-60	0.0-173	4.5-44	4.5-50	7.6-14	50-53	2.6-12	37.3-14	490-52	100-44	360-27	33-42	62-28
ha AC 'b' (12)	5.2-10	1.6-62	49.5-53	1.7-89	0.7-58	0.1-119	4.8-39	2.8-72	8.2-21	37-64	2.9-40	33.2-33	420-27	90-36	490-21	45-35	57-41
ha CM (19)	5.19-18	1.9-53	44.0-51	0.3-146	0.2-132	0.5-120	6.6-77	0.6-132	7.4-56	7-120	3.2-62	22.2-49	300-70	270-56	330-53	39-49	17-84
ha GL hu (1)	4.6-	4.0-	35.0-	0.0-	0.1-	5.7-	22.1-	0.1-	22.2-	1-	7.6-	24.4-	730-	140-	130-	5-	7-
ha FR 'a' (1)	5.1-	2.1-	32.0-	1.3-	0.4-	0.7-	7.9-	1.7-	9.6-	18-	4.7-	23.3-	31-	40-	650-	38-	85-
ha FR 'b' (20)	5.1-15	1.4-122	29.0-60	0.5-132	0.2-131	0.6-86	5.9-49	0.9-120	7.5-43	13-108	3.6-45	23.2-47	430-66	170-65	350-58	50-55	54-66
ha FR 'c' (30)	4.7-9	2.1-57	33.0-62	0.2-179	0.1-135	1.2-47	7.7-36	0.4-148	8.4-29	5-152	4.1-39	19.0-40	310-43	100-67	490-26	42-44	68-39
ha FL (5)	5.5-14	1.5-125	70.0-60	1.1-101	1.4-97	0.0-163	4.6-25	2.5-82	7.1-39	36-63	1.7-58	35.4-29	230-99	290-83	360-70	39-77	29-56
ha LP (9)	5.3-14	2.4-100	47.0-89	0.3-168	0.2-165	0.9-87	5.6-66	1.0-157	7.4-70	7-115	4.7-70	29.1-52	480-65	220-81	200-61	33-70	17-111
ha NT (2)	6.0-4	3.9-108	63.5-30	4.7-93	1.5-0	0.0-0	3.6-16	6.4-70	10.0-50	60-24	2.6-0	40.0-2	240-36	130-6	420-36	35-18	40-16
ha RG (5)	5.6-17	1.9-30	32.0-72	0.4-123	0.2-129	0.0-161	1.6-103	0.6-114	5.6-73	27-87	2.0-41	41.7-51	270-83	450-44	230-74	42-24	10-70
All soils (107)	5.1-14	1.9-95	36.0-63	0.4-142	0.2-134	0.7-108	6.6-59	0.8-126	7.8-46	11-109	3.5-57	23.3-46	360-63	140-82	400-48	40-52	49-67
MG (697)	5.3–14	1.7-226	-	-	-	-	-	1.1–142	7.9-53	-	3.3–112	-	-	-	340–56	38-81	57-90
SA (19)	4.4-20	2.1-167	31.2-96	0.2-160	0.2-98	0.4-81	3.6-68	0.5-139	5.5-52	11-112	2.0-53	-	720-29	320-55	250-57	-	-
PB (94)	5.8-13	-	128.7-58	3.7-96	2.2-103	0.1-156	3.0-69	6.4-90	9.8-61	71-36	1.7-55	-	730-29	960-82	162-52	11-76	-
PE (34)	5.5-17	7.0-241	117.0-73	2.7-106		0.2-207	-	3.0-126	-	-	2.4-196	48.6-31	640-38	170-65	180-69	13-46	12-11

[1] Soil group (number of samples). AC 'a' = 'Yellow' Acrisol Alumic derived from granite and granitoid; AC 'b' = 'Red-Yellow' Haplic Acrisol derived from gneiss; ha CM = Haplic Cambisol derived from banded iron-formation, quartzite, schist, gneiss, granite, granitoid, and mafic rocks; ha GL hu = Haplic Gleysol Humic derived from unconsolidated sediments; ha FR 'a' = 'Yellow' Haplic Ferralsol derived from gneiss; ha FR 'b' = 'Red' Haplic Ferralsol derived from banded iron-formation, mafic rocks, and granitoid; ha FR 'c' = 'Red-Yellow' Haplic Ferralsol derived from gneiss, granite, and granitoid; ha FL = Haplic Fluvisol derived from unconsolidated sediments; ha LP = Haplic Leptosol derived from banded iron-formation, quartzite, schist, gneiss, and phyllite; ha NT = Haplic Nitisol derived from mafic rocks and granodiorite; ha RG = Haplic Regosol derived from gneiss. pH(H₂O) = glass electrode in a 1:2.5 suspension (v/v soil and deionized water); P_M = Mehlich-1 extraction; SB = Ca²⁺, Mg²⁺, Al³⁺ (KCl 1 mol L⁻¹ extraction) + K⁺ and Na⁺ (Melhich-1 extraction); CEC = SB + (H+Al) (extracted by 1 mol L⁻¹ ammonium acetate solution at pH 7); V% = (SB/CEC) × 100; SOM = Walkley-Black method; sand, silt, and clay fractions = sieve-pipette method; MG = soils of Minas Gerais (Souza et al., 2015); SA = soils of Southwestern Amazon (Santos and Alleoni, 2013); PB = soils of Paraíba (Almeida Júnior et al., 2016); PE = soils of Pernambuco (Biondi et al., 2011).

by Nitisols and Acrisols. Low Fe and Al contents were observed in Fluvisols, and a high coefficient of variation. In general, highest metal(loid) concentrations were extracted from Cambisols and Regosols by the Usepa SW-846 method 3051A (Table 4). These soil groups also have the highest coefficients of variation for metal(loid) concentrations. For Nitisols and Acrisols, the coefficients of variation for metal(loid) concentrations were low (Table 4).

The correlation of metal(loid) concentrations extracted by acid digestion with clay and SOM contents was below 0.2 (Figure 2). The weak correlation (r <0.5) can be attributed to the lithological diversity of the RDB and the high number of samples with metal(loid) concentrations below the detectable limit of several elements (Table 4).

Table 4. Descriptive statistics of metal(loid) concentrations extracted by acid digestion, literature data and QRV calculated

| Soil[1]	Ag	As	B	Ba	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sr	V	Zn
									mg L^{-1}									
ha AC 'a' (3)	0.16-72[2]	1.91-78	11.67-34	51.16-85	1.79-115	5.76-65	40.43-101	33.46-64	0.15-143	248.06-70	0.46-163	8.40-116	16.81-80	0.08-178	0.77-61	8.35-119	64.90-61	37.45-37
ha AC 'b' (12)	0.39-40	1.30-51	8.2-43	56.86-103	0.23-88	3.43-116	69.93-81	14.67-99	0.10-139	208.21-110	0.63-141	24.01-49	8.70-82	0.02-155	0.53-76	12.87-59	44.48-41	34.80-57
ha CM (19)	0.23-172	12.26-192	1.47-127	40.99-109	5.44-93	7.26-144	92.40-105	31.70-91	0.08-269	170.63-260	4.44-61	33.16-75	16.70-148	0.56-299	0.02-160	10.60-73	71.12-74	45.03-63
ha GL hu (1)	0.23-	0.83-	1.35-	19.00-	3.76-	0.26-	12.68-	5.01-	0.03-	0.77-	4.74-	1.82-	11.03-	0.14-	0.02-	8.65-	5.32-	4.71-
ha FR 'a' (1)	0.55-	7.59-	19.20-	17.03-	0.23-	2.43-	50.62-	6.38-	1.70-	56.95-	2.36-	14.07-	17.08-	0.13-	1.10-	8.64-	149.18-	43.68-
ha FR 'b' (20)	0.23-30	2.83-255	3.99-104	32.29-76	5.02-94	7.82-123	86.15-249	34.36-88	0.21-94	243.72-146	2.36-69	24.91-177	21.11-42	0.79-117	0.28-156	6.45-89	92.51-100	36.36-47
ha FR 'c' (30)	0.37-176	1.99-159	10.6-71	27.81-128	0.23-133	5.47-65	91.75-188	33.06-77	0.23-95	81.43-214	2.36-91	15.31-87	14.14-100	0.13-277	0.81-116	6.84-139	108.20-66	29.37-47
ha FL (5)	0.23-0	1.01-142	5.62-62	155.69-64	2.34-98	12.46-103	57.49-127	46.12-51	0.04-79	368.12-105	0.46-117	17.36-117	20.48-43	0.18-175	0.28-104	8.06-67	71.91-73	70.18-62
ha LP (9)	0.23-0	2.62-148	0.28-163	24.79-160	5.44-59	6.48-114	17.20-160	26.61-147	0.11-77	87.56-110	4.90-55	5.38-100	11.22-69	0.28-116	0.02-212	9.84-70	20.84-198	19.10-89
ha NT (2)	-	0.30-75	8.73-25	134.25-27	1.65-14	10.74-52	55.33-6	38.12-27	0.08-78	410.05-85	0.46-0	18.83-50	13.30-34	0.11-74	0.26-58	14.29-77	64.27-19	47.97-50
ha RG (5)	0.23-0	23.64-107	0.28-68	22.78-20	7.45-10	13.96-68	111.68-65	35.81-51	0.08-124	280.98-38	5.06-12	39.93-91	26.06-43	0.33-197	0.02-0	10.38-34	53.47-40	44.96-98
All soils (107)	0.23-180	2.50-317	6.40-92	31.85-116	2.34-103	6.48-130	70.45-227	31.39-90	0.15-622	158.70-323	2.36-89	19.74-140	16.57-102	0.19-432	0.48-631	8.07-97	74.85-96	36.05-65
MG (697)	-	17.3-389	8.1-80	51.60-268	1.4-203	4.60-160	72.8-166	31.7-114	0.1-529	189-433	8.3-31	17.8-162	16.10-94	-	-	6.6-312	82.70-96	35.10-83
ES (66)	-	6.8-95	-	-	<0.13	8.64-55	41.07-52	5.57-123	-	131.69-90	1.43-138	6.65-96	8.79-159	-	-	-	80.95-46	22.61-87
PB (94)	<DL	-	-	46.34-100	0.04-200	3.57-122	15.56-136	5.75-120	-	199.33-125	<DL	4.39-186	7.10-67	0.24-160	-	-	-	15.33-65
RN (394)	0.30-115	-	-	32.40-115	0.08-57	8.00-73	17.50-81	6.40-88	-	-	-	10.40-88	8.80-84	0.08-110	-	-	13.60-81	12.30-76
QRV MG	<0.45	8	11.5	93.0	<0.4	6.0	75	49	0.05	-	<0.9	21.5	19.5	0.5	0.5	-	129	46.5
QRV RD MED	0.92	10.00	25.6	127.40	9.36	25.92	281.8	125.56	0.40	634.80	9.44	78.96	66.30	0.76	1.92	32.28	299.40	144.2
QRV RD Q-75	0.42	15.47	12.20	75.96	16.80	11.72	158.36	50.37	0.27	368.12	16.79	36.77	22.84	1.04	0.86	11.63	132.56	49.05

[1] Soil group (number of samples). AC 'a' = 'Yellow' Acrisol Alumic derived from granite and granitoid; AC 'b' = 'Red-Yellow' Haplic Acrisol derived from gneiss; ha CM = Haplic Cambisol derived from banded iron-formation, quartzite, schist, gneiss, granite, granitoid, and mafic rocks; ha GL hu = Haplic Gleysol Humic derived from unconsolidated sediments; ha FR 'a' = 'Yellow' Haplic Ferralsol derived from gneiss; ha FR 'b' = 'Red' Haplic Ferralsol derived from banded iron-formation, mafic rocks, and granitoid; ha FR 'c' = 'Red-Yellow' Haplic Ferralsol derived from gneiss, granite, and granitoid; ha FL = Haplic Fluvisol derived from unconsolidated sediments; ha LP = Haplic Leptosol derived from banded iron-formation, quartzite, schist, gneiss, and phyllite; ha NT = Haplic Nitisol derived from mafic rocks and granodiorite; ha RG = Haplic Regosol derived from gneiss; MG = soils of Minas Gerais (Souza et al., 2015); ES = soils of Espírito Santo (Paye et al., 2010); PB = soils of Paraíba (Almeida Júnior et al., 2016); RN = soils of Rio Grande do Norte (Preston et al., 2014a); QRV MG = soil quality reference value for Minas Gerais (Copam, 2011); QRV MED = soil quality reference value for the Rio Doce Basin calculated by 4 × median; QRV RD Q-75 = soil quality reference value for the Rio Doce Basin calculated by 75th percentile; < DL = below detection limit.
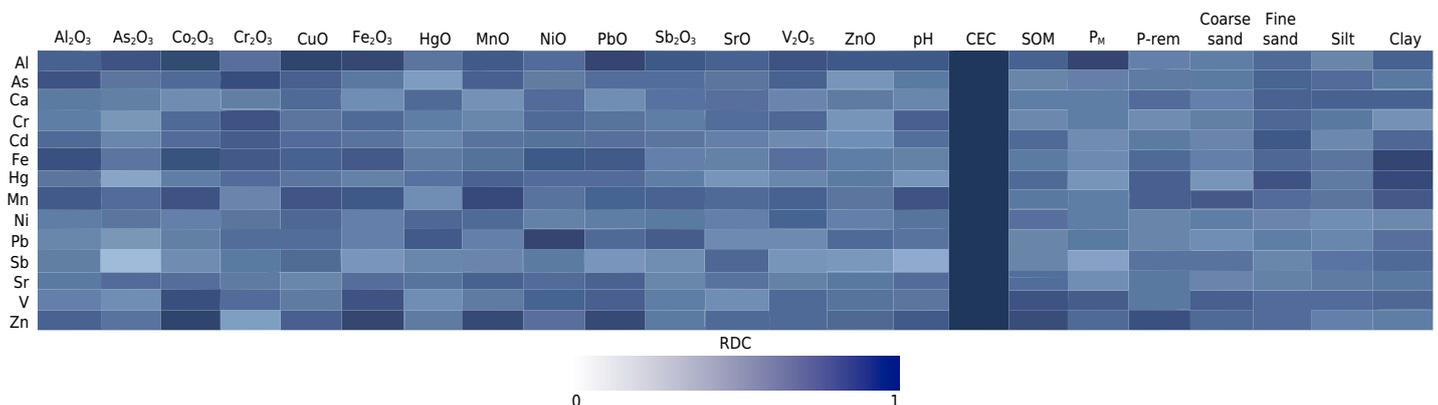
Figure 2. Correlation matrix between metal(loid) concentrations determined by X-ray fluorescence, soil properties, and metal(loid) concentrations extracted by acid digestion.

Principal component analyses are indicated for significantly correlated variables and therefore Ag, B, Cd, Hg, Mo, Sb, and Se concentrations were not considered in the subsequent analyses. Three main components (PCs) with eigenvalues above 1.0, explained together 65.6 % of the variance (Figure 3). Component 4 and higher had eigenvalues below 1.0, which can hardly explain the variance better than the original variables (1/14 = 7.14 %), so they were excluded from subsequent analyses (Wackernagel, 2003; McKillup and Dyar, 2010).

The first component (PC1) explained 38.2 % of the total data variance. The PC1 had high negative loadings for Co, Cr, Cu, Fe, Mn, Ni, V, and Zn (Figure 3). The second component (PC2) accounted for 18.7 % of the total variance and high negative loadings for Al^{3+}, SOM, and clay contents and positive loadings for As concentrations. The third component (PC3) explained 8.7 % of the total variance and was highly correlated to Cr and Pb concentrations. The negative values of PC1 represent soils rich in Fe oxides containing Co, Cr, Cu, Mn, Ni, V, and Zn. Negative values of PC2 are associated with soils with high Al^{3+}, SOM, and clay contents.

Between 40 and 90 % of the variation in metal(loid) concentrations extracted by acid digestion were explained by the variation in the concentrations assessed by XRF (Figure 2). In addition, the correlation matrix indicated that metal(loid) concentrations measured by XRF are explained by K (R^2 between 0.52 and 0.72, except for CaO), Th (R^2 between 0.50 and 0.89, except for Cr_2O_3, Na_2O, and V_2O_5), and eU (R^2 between 0,48 and 0.67, except for V_2O_5), as well as the ratio between the signals and the variables of magnetometry (Figure 4). The soil group, geomorphology, and lithology presented high correlation coefficients (above 0.5) for most elements analyzed by XRF. The correlation coefficients were low for the bioclimatic variables, except for precipitation seasonality and precipitation in the warmest quarter.
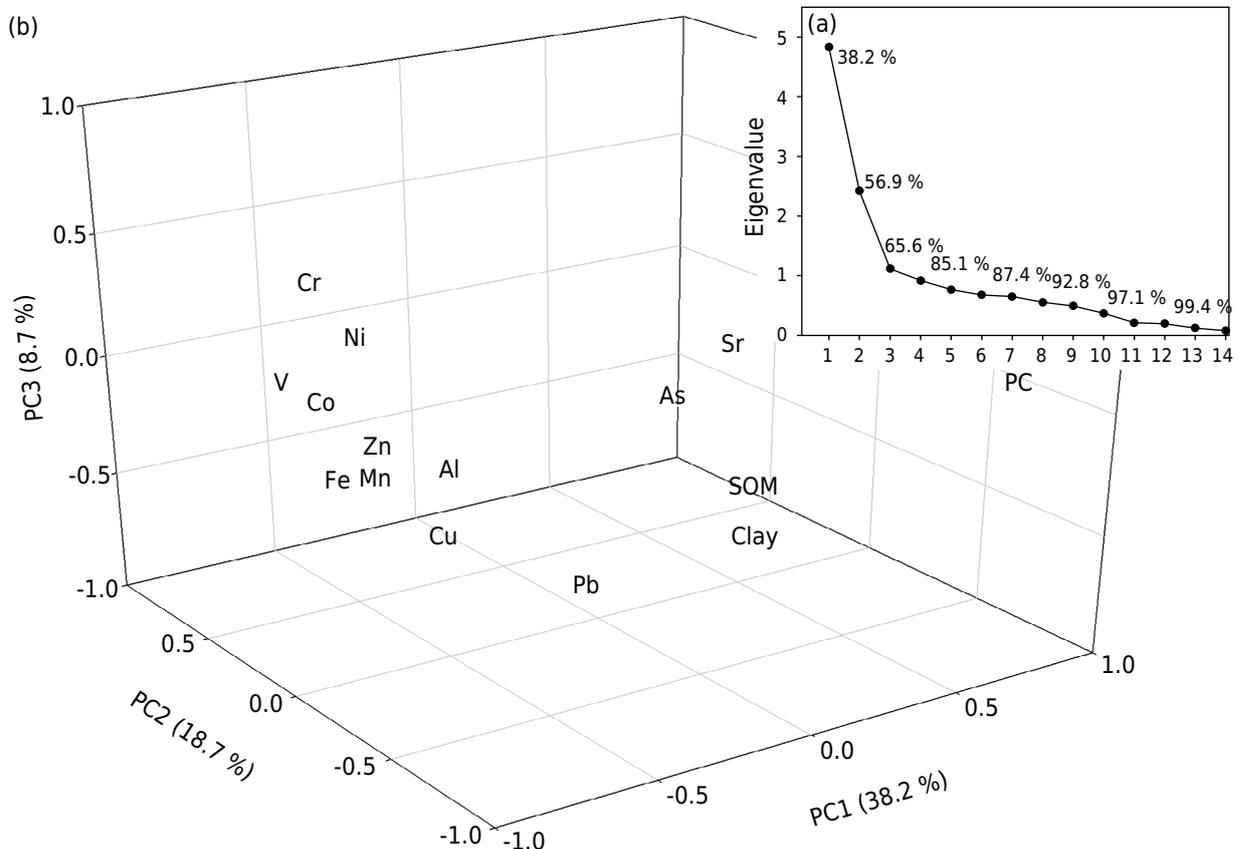
Figure 3. Eigenvalue of correlation matrix and variance explained per PC (a). Projection of the variables on factor plane PC1 × PC2 × PC3 (b).
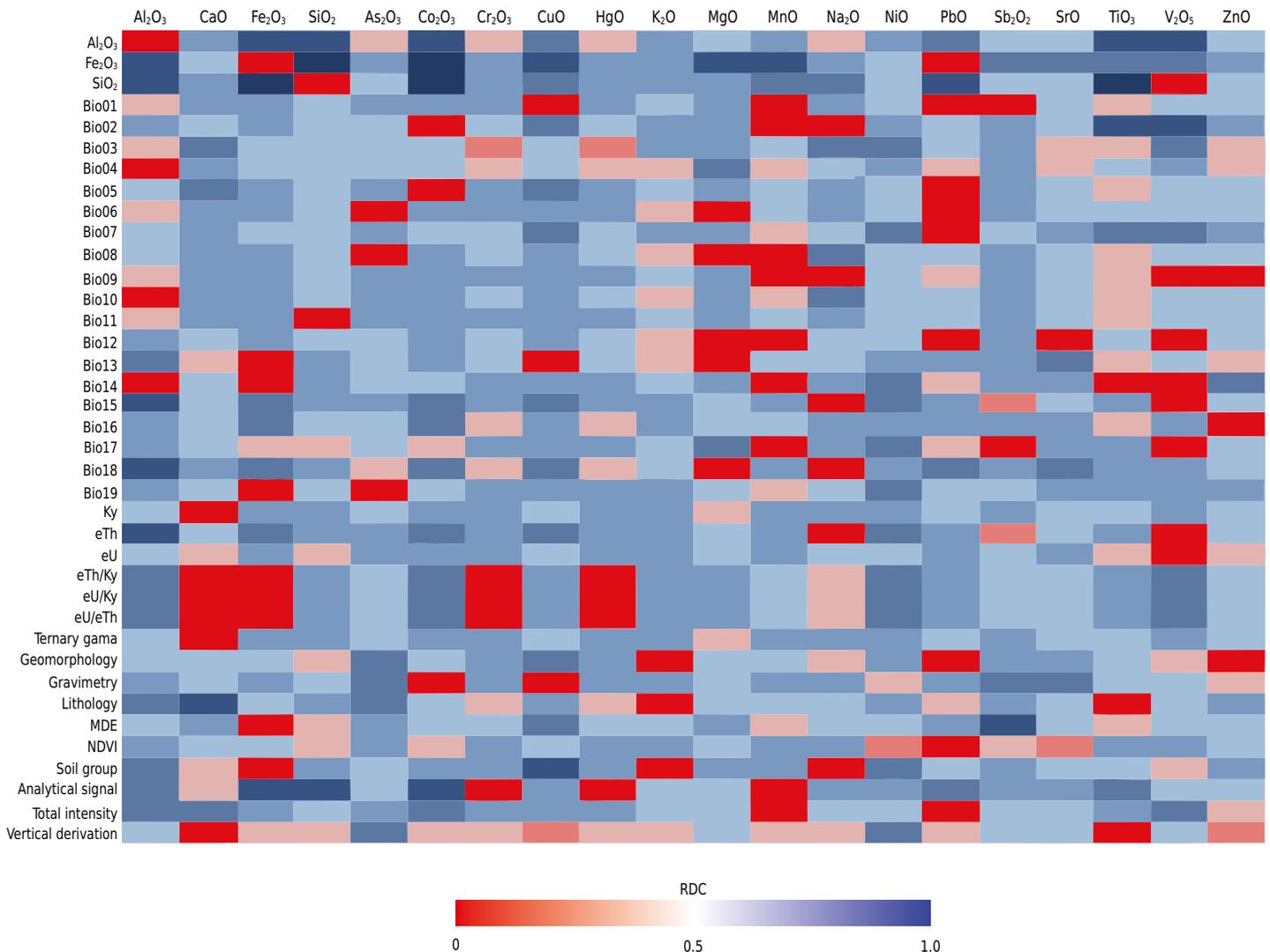
Figure 4. Correlation matrix between metal(loid) concentrations determined by XRF and environmental variables. Bio01 = annual mean temperature; Bio02 = mean diurnal range; Bio03 = isothermality; Bio04 = temperature seasonality; Bio05 = maximum temperature of warmest month; Bio06 = minimum temperature of coldest month; Bio07 = temperature annual range; Bio08 = mean temperature of wettest month; Bio09 = mean temperature of driest month; Bio10 = mean temperature of warmest month; Bio11 = mean temperature of coldest month; Bio12 = annual precipitation; Bio13 = precipitation of wettest month; Bio14 = precipitation of driest month; Bio15 = precipitation seasonality; Bio16 = precipitation of wettest quarter; Bio17 = precipitation of driest quarter; Bio18 = precipitation of warmest quarter; Bio19 = precipitation of coldest quarter.

DISCUSSION

The median values of pH(H_2O), P_M, SOM, CEC, and sand, silt, and clay contents in soils of RDB are similar to reports of previous studies for the states of Minas Gerais (Souza et al., 2015), Espírito Santo (Paye et al., 2010), and São Paulo (Casarini et al., 2001).

Low mean values of P_M, V%, CEC, and P-rem indicate intense weathering under moist tropical climate conditions. Transformation of primary or secondary minerals under wet and freely drained conditions promotes the preferential removal of Si, and Fe and Al accumulation in form of oxides. Soil acidification resulting from weathering and the incorporation of organic material favor base leaching, reduce CEC, and increase specific anion adsorption (Fontes, 2012; Kämpf and Curi, 2012). Despite the intense weathering observed in the soils, the parent material influences the natural fertility, expressed in the values of SB, V%, and CEC (Tables 1 and 2).

Median metal(loid) concentrations in the soil surface layer of the RDB are up to 67 times lower than the median levels recorded in the topsoil of the Iron Quadrangle (Souza et al., 2015), and up to five times higher than in previous studies in other regions of Brazil

(Santos and Alleoni, 2013; Coringa et al., 2014; Preston et al., 2014; Almeida Júnior et al., 2016). These results can be attributed to the abundance of mineralized rocks in the highlands that form the drainage divide of the RDB (Dardenne and Schobbenhaus, 2001).

High coefficients of variation of metal(loid) concentrations are attributed to the geo-pedological diversity in the RDB (Table 1). The coefficients of variation were highest for As, Sb, Se, and Hg, which are closely related to the parent material and sensitive to anthropogenic impacts of mining or air pollution (Kabata-Pendias, 2011; Alloway, 2013).

As observed in other biomes, Al and Fe have the lowest coefficients of variation (Marques et al., 2004; Biondi et al., 2011; Souza et al., 2015; Almeida Júnior et al., 2016). The solubility of these elements during weathering is low and constitute the main secondary minerals of weathered soils (Kabata-Pendias, 2011; Fontes, 2012).

Except for Ag and Ba, the Quality Reference Values (QRV) calculated for the RDB were between 1.03 and 42 times higher than the overall QRV defined for Minas Gerais (Table 3). This result reinforces previous studies that suggest the regionalization of QRV, since the pedological variability cannot be represented by a single geochemical background value (Souza et al., 2015). In addition, QRV calculated for Cd, Cr, and Ni in RDB were 1.2 to 12.9 times higher than the prevention value (concentrations of a particular substance in the soil, above which changes in the soil quality may occur, affecting main soil functions) determined at the national level (Conama, 2013).

High coefficient of variation of metal(loid) concentrations in Leptosols and Cambisols can be explained by the parent material and incipient degree of pedogenesis. In the RDB, these soils are mostly derived from quartzite and banded iron-formation, materials that have different metal(loid) concentrations (Pedrosa-Soares et al., 1994; Dardenne and Schobbenhaus, 2001). Moreover, pedogenesis in these materials is incipient, due to the high weathering resistance and frequency of mass movements. Therefore, the physical and chemical properties and metal(loid) concentrations are strongly associated with their parent material (Santos et al., 2006; Alloway, 2013; WRB, 2014). Metal(loid) concentrations in weathered soils can be attributed in part to the inheritance of the original material, especially in the case of "Red" Haplic Ferralsols derived from banded iron-formation (CPRM, 2003; Souza et al., 2015). In addition, ferralisation favors the relative concentration of metal(loids) associated with iron oxides by adsorption and, or, coprecipitation (Kabata-Pendias, 2011; Alloway, 2013). However, the lower metal(loid) concentrations in Acrisols can be attributed to the lower clay content in the surface horizons of these soils (WRB, 2014).

Metal(loid) concentrations were lowest in flooded soils. Anaerobic conditions in poorly drained soils result in the selection of anaerobic microorganisms that reduce the redox potential. Consequently, the mobility of variable valence elements (such as Cr and As) increases rapidly. Variable-valence metals (Co, Ni, Cu, Pb, and Zn) are affected by dissolution of Fe oxides in flooded soils reduced by oxidation of organic carbon (Zachara et al., 2001; Vodyanitskii and Plekhanova, 2014). The reduction of Fe oxides leads to soil gleization and leaching of Fe and co-precipitated elements (Alloway, 2013).

High correlation between Co, Cr, Cu, Fe, Mn, Ni, V, and Zn, and the antagonism of these with As concentrations, as demonstrated on PC1 and PC3, suggests that rock mineralization occurred simultaneously or in parallel (Figure 3), which occurred at different moments in the formation of As minerals.

Affinity between Al^{3+}, clay, and SOM contents expressed in PC2 indicate the differences between parent material and pedogenesis in the RDB (Figure 3). Soils derived from banded ferriferous formation and other Fe-rich rocks are arranged in elevated portions of the landscape, where frequent erosive processes prevent clay and SOM accumulation. In lower portions of the landscape, where pedogenesis forms deeper soil, SOM is accumulated, and a relative enrichment of Al and clay as products of intense weathering under wet and tropical conditions is observed.

The poor relationship between soil classification and metal(loid) concentrations can be attributed to the diversity of parent materials of each soil group (Table 1). Soils at an initial development stage, such as Leptsols, Regosols, and Cambisols, can be derived from different parent materials, at varying weathering degrees, and arranged in different topographic positions (WRB, 2014). Ferralsols also are derived from different parent materials, reducing the efficiency in the prediction of metal(loid) concentrations according to the soil group. In such cases it would be appropriate to consider soil formation factors for this determination (Jenny, 1941). However, the low correlation coefficients indicate that lithology, relief position, and vegetation cover cannot predict the geochemical behavior of the soil satisfactorily either (Figure 4).

The strong correlation between gamma spectrometry (eTh, K, eU, and their ratios) values and metal(loid) concentrations can be attributed to the inherited contents of the parent material and pedogenesis (Wilford, 2012). Thorium-containing minerals, such as zircon and ilmenite, are more abundant in felsic igneous rocks and gneiss. These minerals are resistant to weathering, favoring the relative Th concentration in acidic and well-drained soils, compared to K and other more soluble elements. Trivalent elements also accumulated in highly weathered soils and/or in silica-cemented horizons, Fe or Al oxides can be predicted by Th-isotope counting (Figure 4). Potassium is a component of the structure of mainly feldspars, biotite, and muscovites, which are found at higher levels in felsic igneous rocks, and gneisses than in mafic rocks (Faure, 1991). In addition, alkali and alkaline earth metals with a hydrated ionic radius similar to K, such as Ba, Co, and Sr, also have similar behavior as K during weathering and are strongly correlated (Figure 4). The increase of Uranium in rocks is directly related to the increase in silica content (Falck et al., 2008). This element occurs as trace element in minerals such as quartz, zircon, monazite, and feldspar, and is relatively abundant in accessory minerals.

Temperature and precipitation are climatic variables usually well correlated with soil properties, and consequently, may be associated with metal(loid) concentrations (Sims and Nielsen, 1986; McKenzie and Ryan, 1999; Hoorn et al., 2010). The weak association between climatic variables and metal(loid) concentrations in the RDB can be attributed to the relative climatic homogeneity of the area, which leads to the weathering of weaker rocks and the persistence of rocks composed of resistant minerals. This condition weakens the correlation of climatic factors with metal(loid) concentrations, and simultaneously reinforces differences in the mineralogical composition of the rocks.

Information about heavy metal concentrations in the mud derived from rupture of the dams is still scarce. A previous study reported higher levels of As (up to 3.33 times), Ba (2.36), Mn (4.96), V (1.36), and Zn (1.53) in the mud, compared to the QRV calculated for the RDB (Guerra et al., 2017).

CONCLUSIONS

Differences between the Quality Reference Values calculated for the Rio Doce Basin and the overall values for the state of Minas Gerais given by the current legislation reinforce the need for regionalization of soil quality values. This strategy is particularly essential in states with a high geo-pedological diversity, since metal(loid) concentrations are determined by the parental material and pedogenesis. Therefore, future regional studies should be developed to establish detailed reference values for the particular soil properties.

The correlations between metal(loid) concentrations inferred by X-ray fluorescence and acid digestion suggest that the method can be used to investigate contaminated areas.

The correlation of gamma spectrometry with metal(loid) concentrations should be explored in future studies for the estimation of these elements in soils.

The study provides data to monitor the areas affected by the rupture of the Fundão tailings dam, as well as possible future environmental impacts.

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