



Geochemistry and spatial variability of metal(loid) concentrations in soils of the state of Minas Gerais, Brazil

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ABSTRACT

Since 2009 a policy has been implemented in Brazil to establish the natural concentrations of potentially toxic substances in soil for each state. Historically a 'mining state', Minas Gerais established a Quality Reference Value for metal(loid)s for all of the soils in the state. To successfully establish these values it is important to study the spatial geochemical diversity for the state. In this context, the objectives of this work are: (1) to evaluate the natural concentrations of metal(loid)s in pristine Minas Gerais soils and (2) to interpret the spatial variability in concentration of these elements. The 0–20 cm layer of soils was sampled for 697 georeferenced sites including the main geological materials and soil groups. Soil properties were analyzed according to methodologies suitable for Brazilian soils. The concentration of metal(loid)s was determined by acid extraction according to EPA 3051A. Descriptive statistics, Pearson correlation and spatial variability analyses were performed. The dominance of acidic pH and low CEC values reflects the pervasive deep acid weathering. The variability of metal(loid) concentrations for soils of the state may be attributed to geological diversity and different pedogenesis. Correlation and spatial analysis indicated that the Fe concentration is strongly associated with metal(loid) concentrations in topsoil. According to the spatial geochemical diversity of the state, a k-means cluster analysis was performed which identified four clusters. A significant difference in the mean values of metal(loid) concentrations between the clusters confirmed that the single Quality Reference Value established does not represent the geochemical diversity of soils in Minas Gerais.

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1. Introduction

Historically Minas Gerais has been known as the most mineral rich state in Brazil. Reserves of precious stones and gold discovered in the 17th century made this region the economic center of the Portuguese province. Currently, large reserves of Al, Au, CaCO₃, Fe, Cr, Cu, Mn, Nb, Ni, Pb, P, Sn and Zn have been identified. Minas Gerais is one of the largest producers of metal and non-metal minerals in Brazil (Dardenne and Schobbenhaus, 2001).

Minas Gerais hosts all thirteen soil groups of the Brazilian Soil Classification System and twelve of the FAO Soil Classification System. The geological materials are also highly diverse. In the northern part of the State, Proterozoic and Paleogene sedimentary rocks partially cover igneous rocks. Proterozoic metamorphic rocks with common plutons occur

in the east and south. In the west, Mesozoic pyroclastic rocks and sedimentary rocks interbanded with mafic igneous rocks occur, conferring a high degree of geological diversity to the state (Moreira and Camelier, 1977; COMIG, 2003).

The Quality Reference Values (QRVs) for metal(loid)s in Minas Gerais soils were established in 2011 (COPAM, 2011). The QRV represents the natural concentration of potentially toxic elements in the soils of the state. These values were obtained by EPA 3051A acid digestion (USEPA, 2007) of topsoil samples for the main rocks of the state. In spite of the geological variability, just one QRV was allocated for As (8 mg kg⁻¹), B (11.5), Ba (93), Cd (0.4), Co (6), Cr (75), Cu (49), Hg (0.05), Mo (0.9), Ni (21.5), Pb (19.5), V (129), and Zn (46.5) for the entire state. A single QRV is of little value and studies of pedogeochemical variance are necessary in Minas Gerais to quantify natural variations in metal(loid) concentrations and improve the monitoring of soil contamination in the state, considering its large area, mining, industrial activities and geo-pedological diversity.

The objective of this study was to assess the concentration and spatial distribution patterns of Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sr, V and Zn in non-contaminated soils of Minas Gerais.

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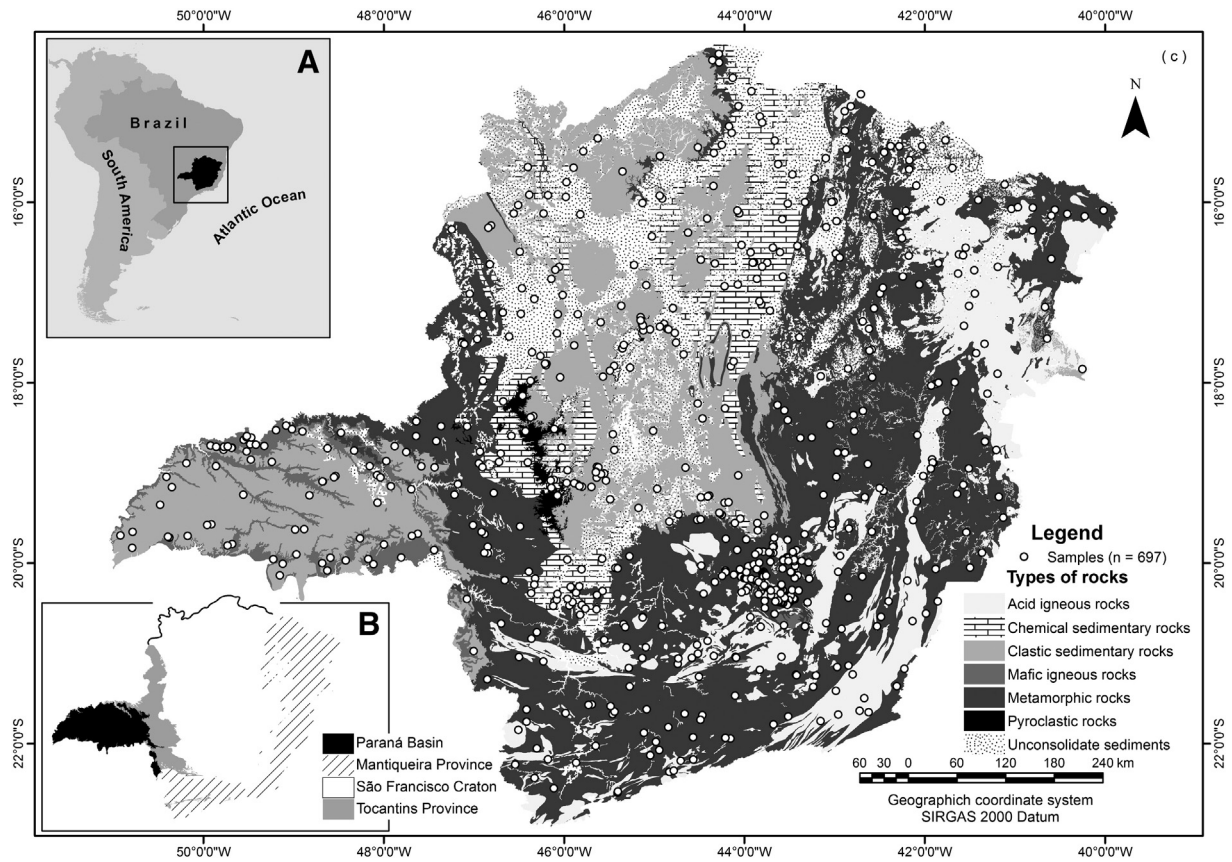


Fig. 1. (a) Location of Minas Gerais state, (b) geological provinces of Minas Gerais, (c) samples collected in study area according to type of rocks.

2. Study area

Minas Gerais in southeast Brazil has a total area of approximately 589,000 km² and particular landscape diversity. Altitudes vary between 250 m, in the São Francisco valley, and 1500 m, in highlands associated with resistant rocks and horst–graben systems. Minas Gerais can be

divided into three climatic regions: i) areas at lower altitudes (in the São Francisco valley), with an average temperature of 23 °C and precipitation below 1200 mm per year; ii) areas at higher altitudes (on and around the highlands), with an average temperature of 20 °C and precipitation above 1800 mm per year; and iii) the rest of state, with a transitional climate between the other two (Nunes and Vicente, 2009).

Table 1

Soil occurrence in the study area.

Soil group ^a	Area (%) ^b	Parent material ^c
'Yellow' Haplic Acrisols Clayic (ha AC ce 'a')	<0.01	Neoproterozoic metapelites
'Red' Haplic Acrisol Clayic (ha AC ce 'b')	3.96	Neoproterozoic gneiss, granitoid, marble and biotite-schist
'Red-Yellow' Haplic Acrisol Clayic (ha AC ce 'c')	7.62	Archean gneiss, granite and metapelites, Paleoproterozoic gneiss and Cretaceous sandstone
Haplic Arenosol Dystric (ha AR dy)	2.77	Neoproterozoic and Cretaceous sandstones
Fluvic Cambisol (fv CM)	0.06	Holocene alluvial beds
Haplic Cambisol (ha CM)	17.09	Neoproterozoic BIF, quartzite, schist, arcosean sandstone, siltstone, claystone, granitoid, Paleoproterozoic granite
Haplic Cambisol Humic (ha CM hu)	0.37	Neoproterozoic migmatite, granite, granitoid and quartzite, Cretaceous alkaline rocks
'Yellow' Haplic Ferrasol Clayic (ha FR ce 'a')	1.44	Paleoproterozoic gneiss and granite, Paleogene sediments, Cretaceous alkaline rocks
'Red' Haplic Ferrasol Clayic (ha FR ce 'b')	29.05	Cretaceous sandstone, mafic, pyroclastic and alkaline rocks, Neoproterozoic limestone and Paleoproterozoic BIF
'Red-Yellow' Haplic Ferrasol Clayic (ha FR ce 'c')	22.93	Paleoproterozoic gneiss and granite, paleogene sediments, Cretaceous alkaline rocks
Haplic Fluvisol (ha FL)	1.83	Holocene alluvial beds
Haplic Gleysol Dystric (ha GL dy)	0.1	Holocene alluvial beds
Haplic Gleysol Humic (ha GL hu)	0.28	Holocene alluvial beds and Cretaceous mafic rocks and sandstones
Haplic Chernozem Clayic (ha CH ce)	<0.01	Neoproterozoic limestone
Voronic Chernozem (vo CH)	<0.01	Neoproterozoic limestone
Haplic Leptosol (ha LP)	9.19	Neoproterozoic claystones, siltstones, BIF, quartzite and schist and Mesoproterozoic phyllite, metasandstone
Haplic Luvisol Chromic (ha LV cr)	0.05	Archean gneiss, Neoproterozoic gneiss and marble
Haplic Nitisol Clayic (ha NT ce 'a')	0.49	Neoproterozoic limestone
'Red' Haplic Nitisol Clayic (ha NT ce 'b')	0.35	Archean gneiss and Neoproterozoic granitoid
Haplic Planosol Dystric (ha PL dy)	0.01	Neoproterozoic limestone
Petric Plinthosol Dystric (pt PT dy)	0.1	Mesoproterozoic and Neoproterozoic schist
Haplic Regosol (ha RG)	<0.01	Archean quartzite, Paleoproterozoic BIF and schist
Rock outcrop	2.31	-

^a FAO (2006).

^b UFV et al. (2010).

^c COMIG (2003).

Table 2
Detection limits (PQL) and reference material analyses expressed as % of nominal analyses.

Element	PQL ^a mg kg ⁻¹	Montana I soil % ^b	Montana II soil
Al	2.04	111	113
As	0.05	106	114
B	2.15	–	–
Ba	0.39	90	100
Cd	0.45	132	104
Co	0.98	100	105
Cr	0.39	100	97
Cu	0.57	102	97
Fe	2.98	99	113
Hg	0.05	112	105
Mn	0.21	89	118
Mo	0.78	–	–
Ni	1.45	95	84
Pb	3.43	104	109
Sr	0.12	–	–
V	0.36	102	103
Zn	0.54	101	112

^a PQL is the concentration at which 75% of the laboratories in an inter-laboratory study report concentrations $\pm 20\%$ of the true value (USEPA, 1987).

^b B, Mo and Sr have no Quality Reference Values.

The state hosts the Tocantins and Mantiqueira Fold Belts, the São Francisco Craton and the Paraná sedimentary basin (Fig. 1). The São Francisco province includes: a) 'Mar de Morros' relief (Sea of Hills), developed in the Archean crystalline rocks, mostly covered by Neoproterozoic limestones and clastic rocks, or covered by Cretaceous sandstones in the north of the state. Neoproterozoic and Cretaceous sedimentary rocks occupy the São Francisco Basin; b) higher surfaces developed on Proterozoic quartzite and Banded Iron Formation (BIF), with the 'Espinhaço' and Iron Quadrangle geologic units. The Mantiqueira province contains cliffs and massifs developed in Proterozoic granites/granitoids and metamorphic rocks, of an Archean geosyncline including units from the Mantiqueira Mountains, the southern Highlands of Minas Gerais and Low Crystalline Plateaus. Cliffs and old massifs in Proterozoic granites/granitoids and schist of the Canastra Geosyncline Arc occur in the Tocantins province. The Paraná sedimentary basin is characterized by a tabular surface area and a geosyncline with Juro-Cretaceous sandstones interspersed with mafic igneous rocks, partially covered by Cretaceous sandstones (Moreira and Camelier, 1977; Pedrosa-Soares et al., 1994).

In Minas Gerais deep and highly weathered soils dominate, with Ferralsols (correlate to Latossolos in the Brazilian Soil Classification System) and Acrisols (Argissolos) representing 65% of the state area (Table 1).

3. Material and methods

3.1. Sampling and chemical analysis

Approximately one soil sample was collected every 38 km² on an irregular grid, resulting in a total of 697 geo-referenced sites. The topsoil layer (0–20 cm in depth) was collected, equivalent to the A horizon for the majority of soils. Each sample is composed of five subsamples, collected in the form of a compass (North, South, East and West, all of them spaced apart by 3 m from one sample in the middle of the compass). Sampling was avoided in areas close to potential sources of contaminants (roads, railroads, urban and industrial developments, mining areas and pastures) and stainless steel equipment was used for collecting samples and sample preparation.

The soil samples were air-dried and passed through a stainless steel 10 mesh (2.0 mm) sieve previous to analysis of texture and exchange capacity of soil. Soil pH was measured with a glass electrode in a 1:2.5 suspension of soil in deionized water. Exchangeable acidity ($H^+ + Al^{3+}$) was extracted in a solution of 1 M ammonium acetate at pH 7. Exchangeable Ca^{2+} , Mg^{2+} and Al^{3+} were determined in a 1 M KCl solution. Exchangeable K^+ and Na^+ were extracted by the Mehlich-1 solution. From these results, the sum of the bases (SB) and the cation exchange capacity (CEC) were calculated for each sample. Extractable phosphorus (P_M) was determined in a Mehlich 1 solution. Total soil organic matter (SOM) concentration was determined following the Walkley–Black method. The clay concentration (C_p) was determined by the sieve–pipette method, after dispersion with 0.1 M NaOH (EMBRAPA, 1997).

The samples were crushed and sieved through a 200 mesh prior to acid digestion. Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sr, V and Zn concentrations were determined with an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) in five laboratories following the EPA 3051A digestion method (USEPA, 2007). Satisfactory analyses (deviation below 20%) were obtained for the Montana I Soil and Montana II Soil standard reference materials using there analytical techniques. All Practical Quantification Limits calculated were lower than the Quality Reference Value for Minas Gerais soils (Table 2).

Table 3
Descriptive statistics (median–coefficient of variation) of topsoil properties for 20 soil groups in Minas Gerais State.

Soil Group (n)	pH	P_M mg dm ⁻³	SB cmolc kg ⁻¹	CEC	SOM %	C_p	Al g kg ⁻¹	Fe	Mn mg kg ⁻¹
ha AC ce 'a' (1)	5.8	4.9	7.3	12.7	6.1	29.0	278	23.9	451
ha AC ce 'b' (18)	5.7–8	1.6–12	4.5–78	7.6–38	2.6–114	34.0–36	54.5–42	38.5–48	206–189
ha AC ce 'c' (54)	5.5–13	1.8–187	3.4–96	8.2–40	3.2–81	33.5–45	46.5–58	35.4–72	207–129
ha AR dy (17)	5.3–10	2.0–91	0.3–70	3.8–79	1.0–130	12.2–83	11.2–86	7.5–97	34.4–195
ha CH ce (1)	6.4	1.3	13.0	16.5	4.7	40.0	28.7	37.0	690
vo CH (1)	8.0	19.9	19.6	19.6	17.4	38.0	35.5	37.7	387
ha CM hu (3)	4.0–3	1.5–53	0.4–62	8.3–43	16.0–49	33.7–43	69.0–6	48.3–8	238–82
ha CM (85)	5.3–14	1.6–285	1.1–125	7.2–65	3.5–130	26.1–52	44.7–110	38.7–59	311–434
ha FL (20)	6.2–17	7.7–120	5.3–88	7.7–53	2.3–157	23.0–65	26.8–131	31.1–56	339–72
ha FR ce 'a' (20)	5.1–20	1.5–144	0.6–136	8.1–46	2.7–116	38.0–55	43.6–61	38.6–67	148–106
ha FR ce 'b' (228)	5.3–13	1.8–215	1.1–143	8.3–49	3.5–117	49.5–50	79.2–73	42.6–77	200–217
ha FR ce 'c' (171)	4.1–14	1.5–163	0.5–201	7.9–51	3.4–78	42.5–49	61.5–77	39.2–66	110–147
ha GL hu (6)	5.1–10	2.8–187	1.1–93	11.0–75	6.7–101	14.8–97	36.7–112	14.0–98	30.9–177
ha GL dy (5)	5.0–4	3.9–68	1.3–107	9.3–27	3.2–70	71.0–48	20.8–81	12.3–27	18.4–49
ha LP (52)	5.4–12	2.4–112	1.3–113	7.5–56	3.9–73	22.0–59	49.6–123	25.6–110	385–180
ha LV cr (2)	4.3–2	0.5–16	0.3–141	7.5–33	2.5–57	43.5–57	53.1–54	29.6–50	60.3–32
ha NT ce 'a' (9)	5.2–14	2.2–51	3.2–8	10.1–24	3.5–106	41.5–31	46.5–51	47.0–41	261–79
ha NT ce 'b' (7)	6.4–13	0.9–134	8.9–70	12.8–51	2.8–48	39.0–32	35.7–37	33.7–70	609–58
ha RG (6)	5.6–20	1.0–45	1.5–70	5.6–7	2.0–18	16.0–89	55.4–75	34.5–50	461–69
ha PL dy (4)	4.6–9	1.2–73	0.1–186	6.3–27	2.6–66	48.5–38	53.4–47	40.9–68	43.3–111
All soils (697)	5.3–14	1.7–226	1.1–142	7.9–53	3.3–112	34.0–56	57.1–90	38.0–81	189–433

Table 4
Descriptive statistics (median-coefficient of variation) of metal(loid) concentrations (mg kg⁻¹) extracted by acid digestion in topsoil for 20 soil groups from the state of Minas Gerais.

Soil group (n)	As	B	Ba	Cd	Co	Cr	Cu	Hg	Mo	Ni	Pb	Sr	V	Zn
ha AC ce 'a' (1)	3.6	8.4	178.6	1.4	3.8	14.0	48.0	0.2	0.5	5.3	36.5	18.1	23.1	30.7
ha AC ce 'b' (18)	1.4–163	8.9–67	43.9–125	0.7–194	6.9–91	92.0–62	23.4–72	0.1–134	<PQL	24.4–61	14.9–58	7.9–87	60.4–66	36.6–52
ha AC ce 'c' (54)	2.1–207	8.0–75	85.7–112	1.4–114	7.5–97	56.4–100	34.2–89	<PQL	9.0–15.9	17.6–90	21.8–60	8.2–268	65.1–75	36.7–61
ha AR dy (17)	0.8–107	1.2–133	6.8–176	0.6–89	0.8–290	25.0–78	14.3–84	<PQL	<PQL	7.4–83	4.7–115	0.9–157	16.9–90	7.8–136
ha CH ce (1)	6.5	5.4	95.0	2.0	16.8	62.1	51.0	0.2	23.1–	31.7	15.8	62.4	41.1	<PQL
vo CH (1)	5.2	12.7–	81.2	1.7	7.4	56.8	44.4	0.2	20.1–	23.6	72.6	57.5	42.6	<PQL
ha CM hu (3)	1.7–148	13.3–76	36.4–48	<PQL	5.3–52	20.3–24	34.3–11	0.3–115	<PQL	54.2–7	8.4–120	3.7–74	106–32	46.5–52
ha CM (85)	5.0–291	73.3–91.7	80.9–148	0.8–132	6.1–140	67.0–177	37.1–92	<PQL	5.6–44.6	23.1–154	16.7–111	6.1–113	74.1–74	45.6–71
ha FL (20)	2.3–189	6.5–86	103–60	1.3–71	7.0–68	43.2–90	29.9–51	<PQL	<PQL	16.3–69	12.4–91	13.4–154	51.3–63	44.3–90
ha FR ce 'a' (20)	3.8–173	6.8–74	42.6–170	1.2–82	2.3–140	56.9–71	29.1–129	0.1–208	7.5–120.3	12.6–86	14.1–75	8.4–136	74.3–63	29.2–97
ha FR ce 'b' (228)	5.4–430	10.1–76	50.4–319	1.5–155	4.6–162	108–154	39.0–106	0.1–343	9.0–21.5	21.7–155	17.9–94	6.3–331	168–76	40.3–87
ha FR ce 'c' (171)	2.5–400	8.9–68	32.7–132	0.7–292	3.1–146	58.2–91	22.5–86	0.1–138	10.6–33.4	13.3–96	14.2–83	6.2–164	79.9–74	29.1–62
ha GL dy (6)	0.3–123	2.2–57	44.0–112	<PQL	1.0–200	40.3–78	16.4–102	<PQL	<PQL	11.1–137	5.6–132	4.3–70	41.6–102	17.9–89
ha GL dy (5)	0.6–83	3.2–21	24.5–78.2	<PQL	<PQL	74.0–47	26.8–70	<PQL	<PQL	10.4–68	9.9–128	1.9–68	25.8–91	12.3–73
ha LP (52)	5.6–199	7.9–92	55.9–98.1	<PQL	6.3–150	50.2–200	29.4–83	<PQL	<PQL	17.5–205	<PQL	6.2–87	53.7–125	53.0–65
ha LV cr (2)	5.3–59	5.0–47	29.8–83.4	1.3–33	1.8–84	24.1–8	23.3–27	<PQL	1.8–53.8	5.4–74	7.8–61	12.5–93	52.5–44	13.5–41
ha NT ce 'a' (9)	3.5–87	7.1–81	44.5–124.3	1.6–90	5.3–95	64.0–79	34.7–58	<PQL	<PQL	15.8–68	28.5–51	7.9–104	100–37	30.3–71
ha NT ce 'b' (7)	1.5–129	10.3–65	122–35.2	1.8–118	14.7–74	57.6–96	37.6–94	<PQL	<PQL	25.6–111	16.5–29	16.5–47	66.4–86	63.9–40
ha RG (6)	14.9–63	10.5–40	115–104.1	<PQL	12.1–88	97.8–48	37.6–77	0.1–112	<PQL	30.0–54	27.3–73	9.2–185	85.1–36	43.8–56
ha PL dy (4)	3.0–44	7.9–50	12.3–165.3	1.3–69	1.1–125	50.4–18	35.4–55	<PQL	<PQL	5.4–97	10.6–77	2.4–126	67.6–12	23.2–67
All soils (697)	17.3–389	8.1–80	51.6–268	1.4–203	4.6–160	72.8–166	31.7–114	0.1–529	8.3–31	17.8–162	16.1–94	6.6–312	82.7–96	35.1–83

Legend: <PQL = concentration values below the Practical Quantification Limit.

3.2. Statistical and geostatistical analyses

Descriptive statistical analyses were performed for all 697 samples, as well as for each of the soil groups. Furthermore, the Pearson correlation was calculated between metal(loid) concentrations and soil properties. The Pearson correlation between metal(loid) concentration and Fe/Cp and SOM/Cp ratios was also calculated.

Principal Component Analysis (PCA) was performed to clarify the correlation between the variables. PCA is a variable reduction method that produces a smaller number of artificial and uncorrelated variables, called Principal Components (PCs). The PCs are listed in decreasing order of explained variance in the data. Prior to PCA, analytical data were logarithm transformed and standardized (Wackernagel, 2003; McKillup and Dyar, 2010).

Spatial dependence is the statistical relationship between values of the variables measured in samples and the geographical location of these samples. A semivariogram is a tool that can demonstrate spatial dependence of a variable through the relationship between the semivariance of the values and the distance between the sample points. Ideally, semivariance increases with distance to a constant value (sill), at a certain distance (range), beyond which there is no spatial dependence (Goovaerts, 2001). The range value depends on the spatial interaction of a soil process affecting each property with the sampling scale that is used (Cambardella et al., 1994). The semivariance value at a distance of zero (nugget) represents random variability, which is undetectable by the sampling scale.

The nugget to sill ratio expresses semivariance which is not explained, and reflects the strength of spatial dependence. Strong spatially dependent properties are controlled by factors attributed to soil formation and characteristics of soil, such as altitude, parent material and texture (Cambardella et al., 1994).

Autocorrelation of the samples was evaluated by the experimental semivariogram, to which mathematical models were fitted. The mathematical models that were tested included stable, circular, spherical, exponential and Gaussian. The semivariogram model was adjusted according to the normality, stationarity, tendency and anisotropy of the samples. The fitness of the semivariogram model was evaluated by a cross validation technique (Goovaerts, 1997).

Metal(loid) concentrations were interpolated across the whole state using ordinary kriging. The software used for these analyses was PASSaGE® (Rosenberg and Anderson, 2011) and the geostatistical extension of ArcGIS 10.1®.

To examine the homogeneity of metal(loid) concentrations among all soil samples, a cluster analysis was performed using STATISTICA 8.0® software. Cluster validation was executed using stability and validity tests. Statistical significance of clusters was evaluated by analyzing the variance between groups (ANOVA) and by Tukey's HSD post-hoc test (Mooi and Sarstedt, 2011).

4. Results

4.1. Topsoil in the state of Minas Gerais

The topsoil samples in Minas Gerais showed predominantly acidic pH levels and low cation exchange capacity (CEC) values, reflecting a deep weathered scenario under wet and tropical climate (Table 3). The low natural fertility of soils was indicated by the low values of Mehlich-1 extractable P (P_M), the sum of bases (SB) and the soil organic matter (SOM) concentration.

The soils can be defined as clayey (ha AC ce 'c', ha FR ce 'a', ha FR ce 'c', ha GL dy, ha NT ce 'a', ha LV cr, ha NT ce 'b' and ha PL dy), loamy (ha AC ce 'a', ha AC ce 'b', ha CM, ha FL, ha GL hu, ha LP and ha RG) and sandy (ha AR dy) (Table 3).

The highest median metal(loid) concentrations were for 'Red' Haplic Nitisols, Haplic Cambisols and 'Red' Haplic Ferrasols (Table 4). The last

two soil groups had the highest coefficient of variation values for metal(loid) concentrations.

The lowest metal(loid) concentrations in topsoil were in Haplic Arenosol Dystric, Haplic Gleysol and Haplic Luvisol Chromic (Table 4). Excluding Luvisols, these soil groups also had the lowest coefficient of variation values (Table 4).

The metal(loid) concentrations in each soil group showed significant positive correlations with Fe concentration, SOM, Cp, Fe/Cp, SOM/Cp and SB (Fig. 2).

Considering all soil groups together, no soil property registered a strong correlation (>0.5) with the metal(loid) concentrations (data not shown). This result is attributed to the heterogeneity of metal(loid) concentration in the state, evidenced by the high values of the coefficient of variation, and the large sample size, which weakens the correlation values (Strube, 1988).

Two principal components explained 67% of the variance (Fig. 3). PCs with high eigenvalues are assumed to best represent the geochemical variability and characteristics of the data. Components 3 and higher returned eigenvalues below 1.0 and hardly explain more variance than any of the original variables taken alone ($1/22 = 4.5\%$), so they were excluded from further interpretation (Wackernagel, 2003; McKillup and Dyar, 2010).

The first component (PC1) explained 46.59% of total variance of the data. PC1 is largely composed of original variables which express the soil reactivity, which are Fe concentration, Cp, CEC and SOM. The second component (PC2) explained 20.99% of the total variance, and is mainly composed of original variables which express the stage of weathering, which are SB, pH and Al concentration (Fig. 3). The antagonism between SB and Al concentration shown by PC2 expresses a difference between moderately and highly weathered soils.

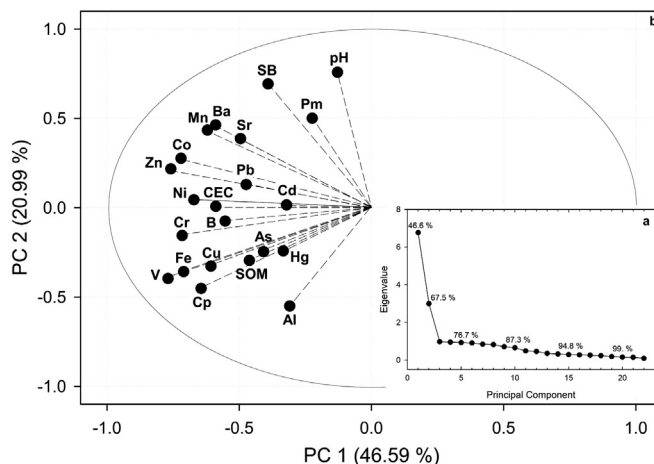


Fig. 3. (a) Eigenvalues of correlation matrix and explained variance per PC. (b) Projection of the variables on the factor plane PC1 × PC2.

PC2 also shows the antagonism between bivalent elements (Ba, Mn, Sr, Co, Zn and Ni) and trivalent elements (Al, As, B, Cr, Fe and V). This antagonism could be associated with relative retention of trivalent elements compared to the leaching out of divalent elements during the process of weathering.

4.2. Characterization of spatial variability

Spatial dependence and anisotropy existed for all metal(loid)s and soil properties (Table 5). The cross-validation indicated satisfactory

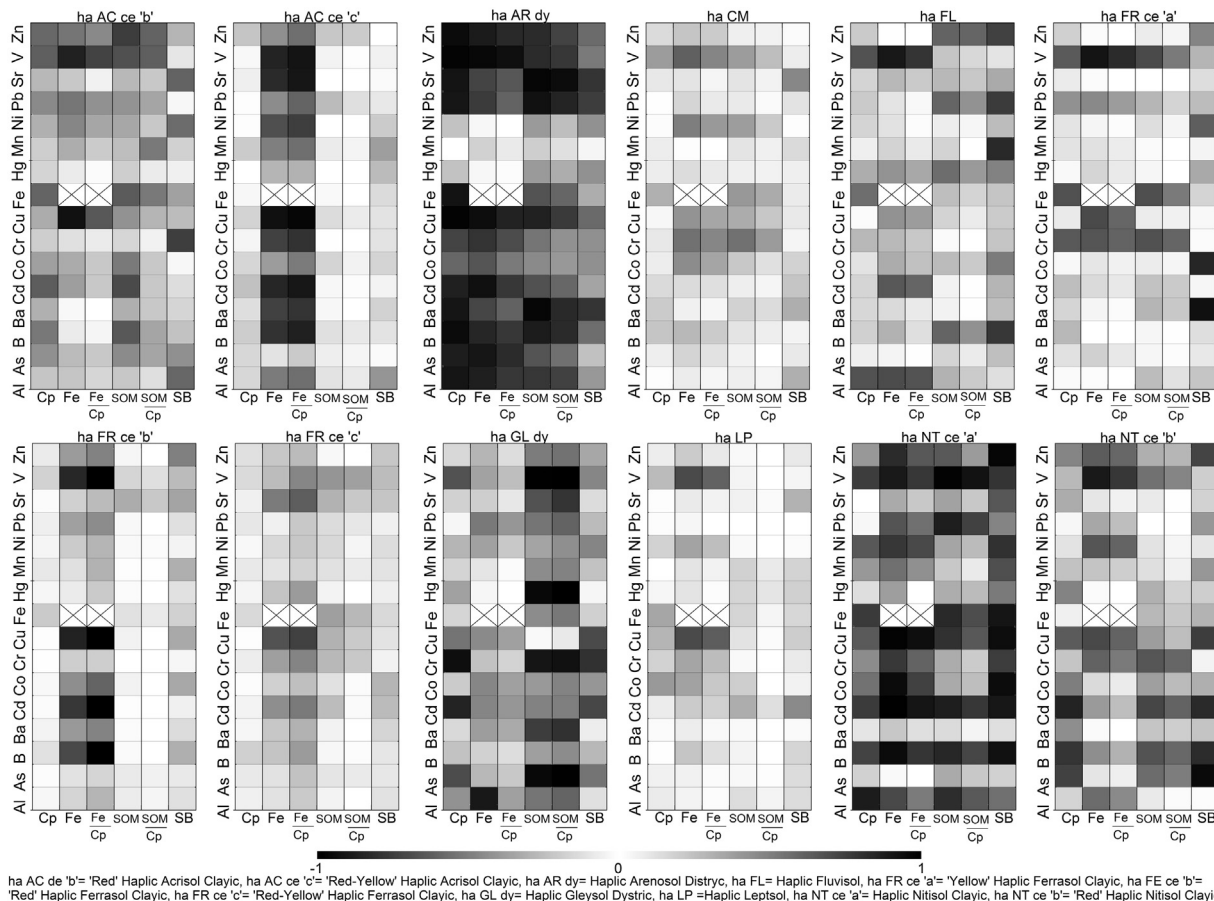


Fig. 2. Correlation between metal(loid) contents and soil properties. Legend: Black dot = correlation with Cp, white dot = correlation with Fe content, dark gray dot = correlation with SOM, gray dot = correlation with CEC.

Table 5

Theoretical models and estimated parameters of the experimental semivariograms and their cross validation statistics.

Properties	Parameters					Estimate ^c	
	Model ^a	Range (km)	Sill	Nugget	Sd ^b	MSE	RMSSE
Cp (%)	C	2.2	436	171	39.2	0.002	1.09
SOM (%)	S	0.1	0.6	0.2	33.3	0.001	0.89
P _M (mg dm ⁻³)	G	3.2	121	40	32.6	0.001	1.41
CEC (cmolc kg ⁻¹)	S	0.1	0.7	0.1	17.9	0.114	0.48
SB (cmolc kg ⁻¹)	C	0.2	8.3	3	33.7	-0.002	1.23
Al (g kg ⁻¹)	S	0.3	1.2	0.1	8.3	0.117	0.40
As (mg kg ⁻¹)	S	181	2.1	1.1	52.4	0.026	1.14
B (mg kg ⁻¹)	St	6.5	83	15.7	18.9	0.001	0.77
Ba (mg kg ⁻¹)	St	10.1	1.3	0.5	38.5	-0.107	1.13
Cd (mg kg ⁻¹)	St	0.3	1.2	0.0	0.1	-0.129	1.60
Co (mg kg ⁻¹)	St	23.9	1.4	0.5	35.7	-0.095	1.32
Cr (mg kg ⁻¹)	E	17.7	0.9	0.4	44.4	0.031	0.75
Cu (mg kg ⁻¹)	E	0.1	0.8	0.3	37.5	-0.065	0.94
Fe (g kg ⁻¹)	E	0.7	0.6	0.1	16.7	-0.005	0.81
Hg (mg kg ⁻¹)	C	0.1	2.3	0.9	39.1	-0.223	4.27
Mn (mg kg ⁻¹)	E	0.2	2.7	1.3	48.2	-0.017	1.41
Mo (mg kg ⁻¹)	S	0.2	2.2	0.7	31.8	-0.028	1.05
Ni (mg kg ⁻¹)	C	14.0	2.1	0.8	38.1	0.065	0.48
Pb (mg kg ⁻¹)	E	3.4	0.5	0.2	40.0	-0.141	1.49
Sr (mg kg ⁻¹)	E	1.4	2.1	0.6	28.6	-0.237	2.88
V (mg kg ⁻¹)	G	0.5	0.9	0.6	66.6	0.008	0.74
Zn (mg kg ⁻¹)	St	0.1	0.4	0.1	25.0	-0.109	1.23

^a C = Circular; E = exponential; G = Gaussian. S = spherical; St = stable.

^b Spatial dependence (%) = (nugget/sill)*100.

^c Error prediction estimated by cross-validation using Mean Standardized Error (MSE) and Root-Mean-Square Standardized Error (RMSSE) (Goovaerts, 1997).

results for interpolation, indicating that the sampling and the theoretical models are well fitted to the field variability; the Mean Standardized Error (MSE) values are close to zero and Root-Mean-Square Standardized Error (RMSSE) values are close to one (Goovaerts, 2001).

All metal(loid)s and soil properties recorded high or moderate degrees of spatial dependence (nugget / sill < 75%) (Table 5).

The spatial distribution of soil properties was influenced by parent material and other soil formation factors at different levels. The SOM values increased in accordance with rising altitude (Fig. 4). The contribution of increased altitude to SOM is well known, it is due to declining temperature and an increase in saturation of soil pores by water, reduced drainage and other causes (Sims and Nielsen, 1986; Tate, 1992). The high values of CEC and SB were concentrated in basalt or limestone areas for which precipitation is below 1200 mm per year (Fig. 4).

The spatial distribution of clay, P_M, Al and Fe concentrations in soils is clearly associated with parent material (Fig. 4). The lowest values of Cp occur in soils on Proterozoic and Cretaceous sandstones in the São Francisco Basin and on Proterozoic quartzite in the Iron Quadrangle. The higher values of P_M occur in soils derived from limestone and mafic rocks, which are naturally rich in P (Rocha Araújo et al., 1992). The highest Al concentrations in soils are associated with in situ bauxite deposits derived from weathering of acid igneous rocks (in the west of state) and colluvial and in situ bauxite deposits derived from acid igneous and metamorphic rocks (in the southeast) (Schobbenhaus and Coelho, 1988). The highest values of Fe and Mn concentrations are in soils derived from mafic rocks (in the west) and BIF (in the center). The lowest Fe concentrations are in sandstone areas, in the north (Fig. 4).

Apart from Pb, the metal(loid) concentrations present similar spatial distribution patterns to the Fe concentration and a high spatial contiguity of concentrations (Fig. 5). The areas for which metal(loid) were above the Quality Reference Value for Minas Gerais (COPAM, 2011) were between 16% and 98% of the state, depending on the element (Fig. 5).

4.3. Cluster analysis

The soil geochemical diversity and the spatial contiguity of metal(loid) concentrations suggest that the regionalization of soil Quality Reference Values in Minas Gerais rather than one universal value for each metal(loid). For the spatial distribution of metal(loid) concentrations four clusters were identified by k-means cluster analysis.

Due to the low correlation among metal(loid)s in the entire non-discriminated data set, all elements were considered on the bases of cluster analysis. The concentrations were standardized to avoid the effect of different scales of variables.

At least 80% of each cluster was kept when the dataset was split into two halves and the two subsets analyzed separately, using the same parameter settings. The mean values of clusters before and after the split did not differ significantly at $\alpha = 0.5$, confirming the stability of clusters.

Clay fraction concentration was utilized to validate the cluster solution. All clusters exhibit significantly different mean values of clay concentration according to ANOVA, indicating that the clusters are distinct groups (Table 6).

The four cluster groups for the soil groups based on parent material consist of the following: i) Granite–Gneiss Terrain cluster, including Ferrasols and Acrisols derived from gneiss; Ferrasols, Cambisols and Acrisols derived from acid igneous rocks, Cambisols derived from schists; Ferrasols derived from limestone and Fluvisols; ii) clastic cluster, including 'Yellow' Haplic Ferrasols derived from unconsolidated sediments; 'Red' Haplic Ferrasols and Haplic Arenosols derived from clastic sedimentary rocks and 'Red' Haplic Ferrasols derived from pyroclastic rocks; iii) Iron Quadrangle cluster, including Haplic Cambisols, 'Red' Haplic Ferrasol and Haplic Leptsols derived from BIF; and iv) Serra Geral cluster, including 'Red' Haplic Ferrasols and Nitisols derived from mafic rocks of the Serra Geral Formation. The soils of Iron Quadrangle and Serra Geral clusters have the highest mean metal(loid) concentrations and the Clastic cluster has the lowest concentrations (Table 6).

With the exception of the Iron Quadrangle cluster, the Mn, Mo, As and Hg mean concentrations were not significantly different between all clusters (Table 6). Previous studies related As and Hg anomalies to both lithology and to historical and recent mining and smelting activities in the Iron Quadrangle (Deschamps et al., 2002; Windmüller, 2007). All other elements were significantly different between at least two clusters, according to ANOVA followed by Tukey's HSD post-hoc test. These results suggest that each cluster should have a particular QRV. Although, the Granite–Gneiss Terrains, the Clastic and the Serra Geral clusters could allocate the same QRV for Mn, Mo, As and Hg, the last two highly toxic and particular hazardous to human health.

5. Discussion

5.1. Geochemical characterization of topsoil

The relative diversity of properties related to exchange capacity, granulometry and reactions in soil reflects the diversity of parent materials and the tropical weathering conditions in Minas Gerais. The transformation of primary minerals into amphoteric secondary minerals, acidic pH, and dominance of kaolinite and Fe (hydr)oxides in clay fraction are widespread in Brazilian soils (Kämpf et al., 2009). Despite the intense weathering, parent material influences on clay concentration and cation exchange capacity.

The median values of metal(loid) concentration in the topsoils of Minas Gerais were higher than the values previously observed in Brazilian soil surveys by Marques et al. (2004), Fadigas et al. (2006), Biondi (2010), Paye et al. (2010), Matschullat et al. (2012) and Schucknecht et al. (2012). These results can be attributed to the abundant mineralized rocks of the state (Schobbenhaus and Coelho, 1988).

The high values of the coefficient of variation of metal(loid)s are attributed to the geologic diversity in Minas Gerais (Table 1). The As, Hg and Mn concentrations in the topsoil have the highest values of the coefficient of variation among the elements analyzed. The variability of the concentration of these elements in Minas Gerais could be associated with the dependence of parent material (Alloway, 2013; Kabata-Pendias, 2011), the mining and smelting activities in some regions of the state.

The lowest values of the coefficient of variation are for metal(loid)s which have low solubility and low mobility during the weathering process (Reimann and de Caritat, 1998; Kabata-Pendias, 2011). These metal(loid)s, particularly Al and Fe, are components of the most common secondary minerals formed under wet and tropical climates (Fontes and Weed, 1991).

Metal(loid) concentrations reflect the Fe richness of parent material, during pedogenesis. 'Red' Haplic Ferrasols and 'Red' Haplic Nitisols developed high metal(loid) concentrations and have the highest Fe concentration among all soil groups (Table 3). It appears that Fe (hydr)oxides apparently regulate the metal(loid) concentration in topsoil. It is well known that Fe (hydr)oxides adsorb and co-precipitate with metal(loid)s in soils (Perelomov and Kandeler, 2006; Miguel and Luiz-Silva, 2009; Kabata-Pendias, 2011; Alloway, 2013).

Haplic Cambisols are characterized by an incipient or moderate weathering degree (FAO, 2006), and have the highest concentrations of As, B, Cr, Hg, Ni and Pb. According to Alloway (2013) the concentrations of these metal(loid)s in soils reflect the composition of their parent material.

The lowest metal(loid) concentrations in topsoil are in soils which have relatively low Fe concentrations. Arenosols and Luvisols are derived from metamorphic and sedimentary rocks that are relatively low in Fe. Low metal(loid) concentrations in Haplic Gleysols are associated with reductive dissolution of Fe (hydr)oxides, which favors the leaching of metal(loid)s.

The Gleysols and Arenosols are derived respectively from unconsolidated sediments and clastic sedimentary rocks, which are known to be geochemically highly variable (Middleton, 1960). However, soils with a low Fe concentration (due to a reduction process or not), under wet climate conditions, have low metal(loid) concentration due to lixiviation. Thus, the relative geochemical homogeneity of these soils is attributed to pedogenesis.

The variability of Haplic Cambisol, Haplic Leptsol and 'Red' Haplic Ferrasols is attributed to the diversity of parent materials for these soil groups (Table 1). Haplic Cambisols and Haplic Leptsols are characterized as soils with an incipient weathering degree which can be derived from any parent material (FAO, 2006). Although 'Red' Haplic Ferrasols are deeply weathered soils, in Minas Gerais this group congregates soils derived from limestone, metamorphic rocks, pyroclastic rocks, mafic rocks and unconsolidated sediments (Ker, 1997).

The metal(loid) concentrations in soil groups can be partially explained by differences in parent material and partially by pedogenesis. The highest concentrations are in incipient and deeply weathered soils derived from metal(loid) rich rocks, suggesting the dominance of a parent material influence. On the other hand, the lowest concentrations are in soils derived from rocks which are poor in metal(loid)s and soils under anoxic conditions, the latter indicating the influence of a pedological processes on concentrations of metal(loid)s. The coefficient of variation can be used as a measure of geochemical variability, which will help define the sampling density in further studies.

5.2. Correlation analysis

The significant correlations between soil properties and metal(loid) concentrations suggest that these elements are contained in different

fractions (soil organic matter, CEC and Fe oxides) of the soil (Alloway, 2013). The greatest number of correlation coefficients higher than 0.5 is between Fe and metal(loid) concentrations (Fig. 2), suggesting that Fe (hydr)oxides are the main pool of these elements in tropical soils (Valadares, 1975; Valadares and Catani, 1975; Fontes and Gomes, 2003; Miguel and Luiz-Silva, 2009; Kabata-Pendias, 2011).

The correlation analysis of metal(loid) concentrations and soil properties indicates three patterns: i) soil groups with metal(loid) concentrations strongly correlated with several soil properties; ii) soil groups with metal(loid) concentrations strongly correlated to one specific soil property; and iii) soil groups with metal(loid) concentrations weakly correlated to soil properties. The first pattern includes Haplic Arenosol Dystric, 'Red' Haplic Acrisol, Haplic Fluvisol, 'Yellow' Haplic Ferrasol Clayic, Haplic Nitisol Clayic and 'Red' Haplic Nitisol Clayic. The high correlation values suggest an important role of Cp, SOM, Fe concentration and CEC to maintain metal(loid)s in the soil (Fig. 2).

Several studies have shown a positive correlation between clay and metal(loid) concentrations of soils (Chung and Sa, 2001; Deschamps et al., 2002; Fontes and Gomes, 2003; Kabata-Pendias, 2011).

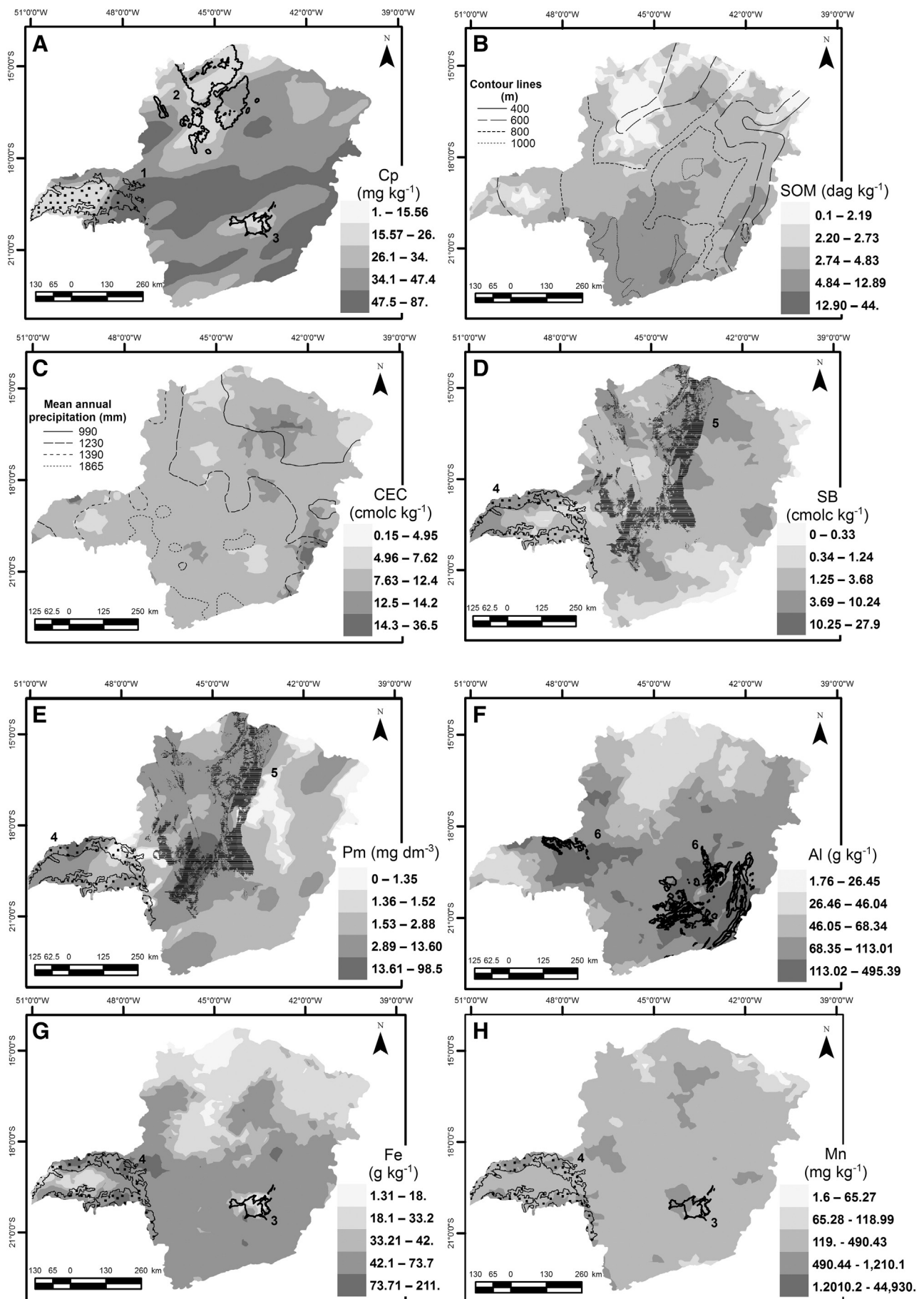
The predominant silicate minerals of highly weathered soils are kaolin minerals, which have minimal substitution of structural cations that would promote a pH-independent exchange capacity. So, the sorption of metal(loid)s by silicate clay minerals is relatively weak and limited in these soils, but the specific adsorption and co-precipitation of metal(loid)s in Fe (hydr)oxides are considered to be dominant form of sorption by the clay fraction (Alloway, 2013).

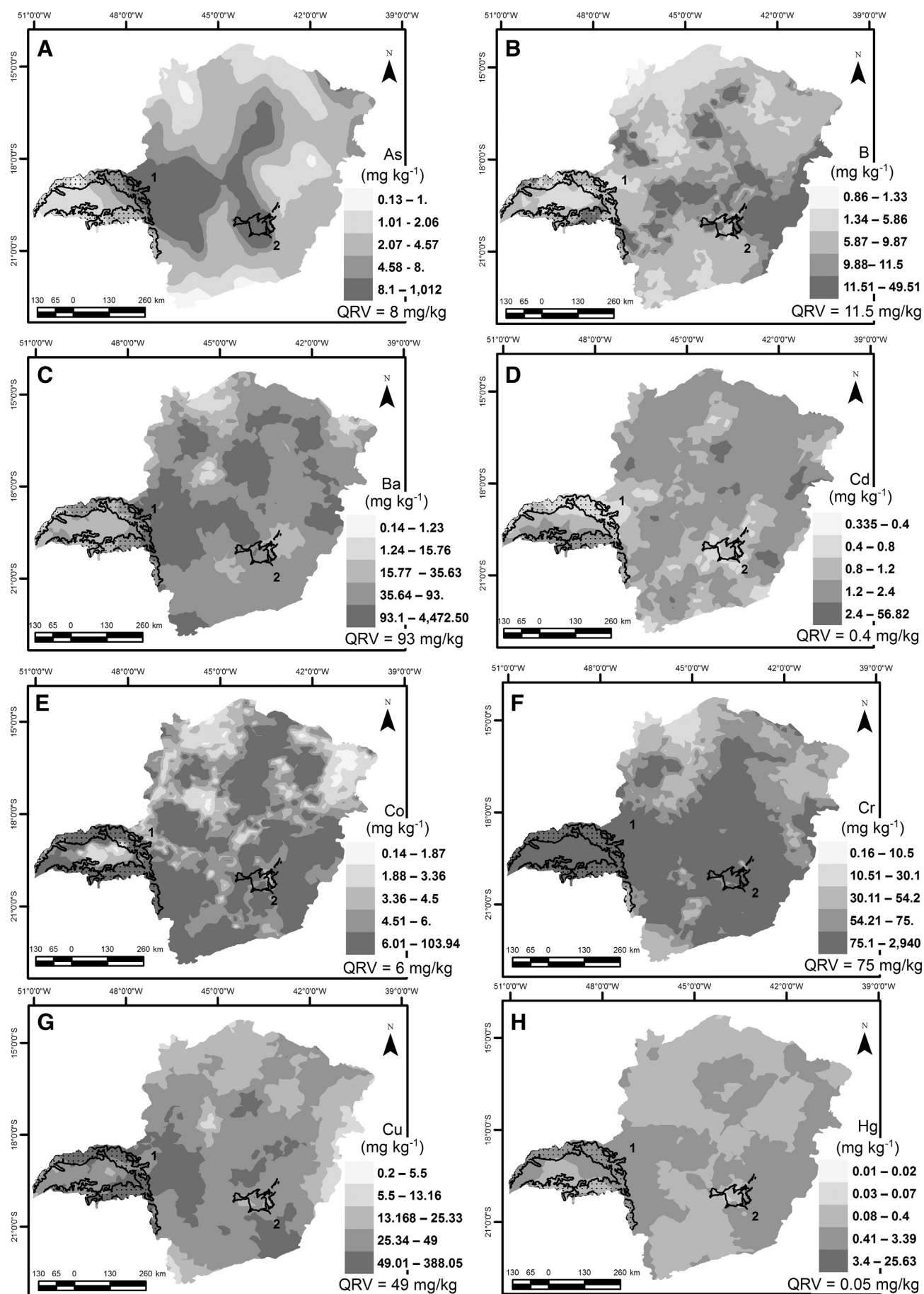
Several studies report the importance of SOM in the scavenging of several elements by mechanisms of electrostatic attraction and complexation (Alloway, 2013). These reactions are especially important in the top layer of soils, where SOM is markedly concentrated.

The second pattern includes 'Red-Yellow' Acrisol, Haplic Gleysol Dystric, 'Red' Haplic Ferrasol Clayic and 'Red-Yellow' Haplic Ferrasol Clayic. These soils showed medium to high correlation values, with the dominance of one soil property highly correlated to metal(loid) concentrations. The concentrations of metal(loid)s in 'Red-Yellow' Acrisol, 'Red' Haplic Ferrasol and 'Red-Yellow' Haplic Ferrasol were highly correlated to Fe concentration, suggesting that Fe (hydr)oxides control the metal(loid) mobility in soil (Perelomov and Kandeler, 2006). On the other hand, the SOM is the most important fraction in the maintenance of metal(loid)s for the anoxic environment of the Haplic Gleysol Dystric (Fig. 2). In soils under reducing conditions, the organic complexation of metal(loid)s apparently becomes the main mechanism for sorption, due to dissolution of Fe(III) minerals and preservation of abundant SOM.

The ratios Fe/Cp and SOM/Cp clarified the difference between the two first patterns (Fig. 2). The first pattern represents soil groups with metal(loid) concentrations strongly correlated with several soil properties, registered weaker correlation values of Fe/Cp and SOM/Cp with metal(loid) concentrations than the original variables Fe concentration and SOM, suggesting that both Fe-oxides and SOM act in the retention of metal(loid)s in soil. This result can be associated with Fe oxide-organic complexes, which help to stabilize the organic matter in the topsoil, but further studies are needed to conclude that. Especially in sandy soils, Fe and Al play an important role in retaining organic matter such as sesquioxide-organic complexes, hindering their decomposition or migration downward (Horbe et al., 2004; Fritsch et al., 2005; Fritsch et al., 2007; Quesada et al., 2011). Previous studies indicated that association between organic matter and Fe (hydr)oxides is more pronounced in clayey soils, such as Haplic Nitisol Clayic and 'Red' Haplic Nitisol Clayic (Dick et al., 2005; Dalmolin et al., 2006).

Among soil groups following the second group, Haplic Gleysol Dystric showed stronger and weaker correlations, respectively, for SOM/Cp and Fe/Cp versus metal(loid) concentrations than original





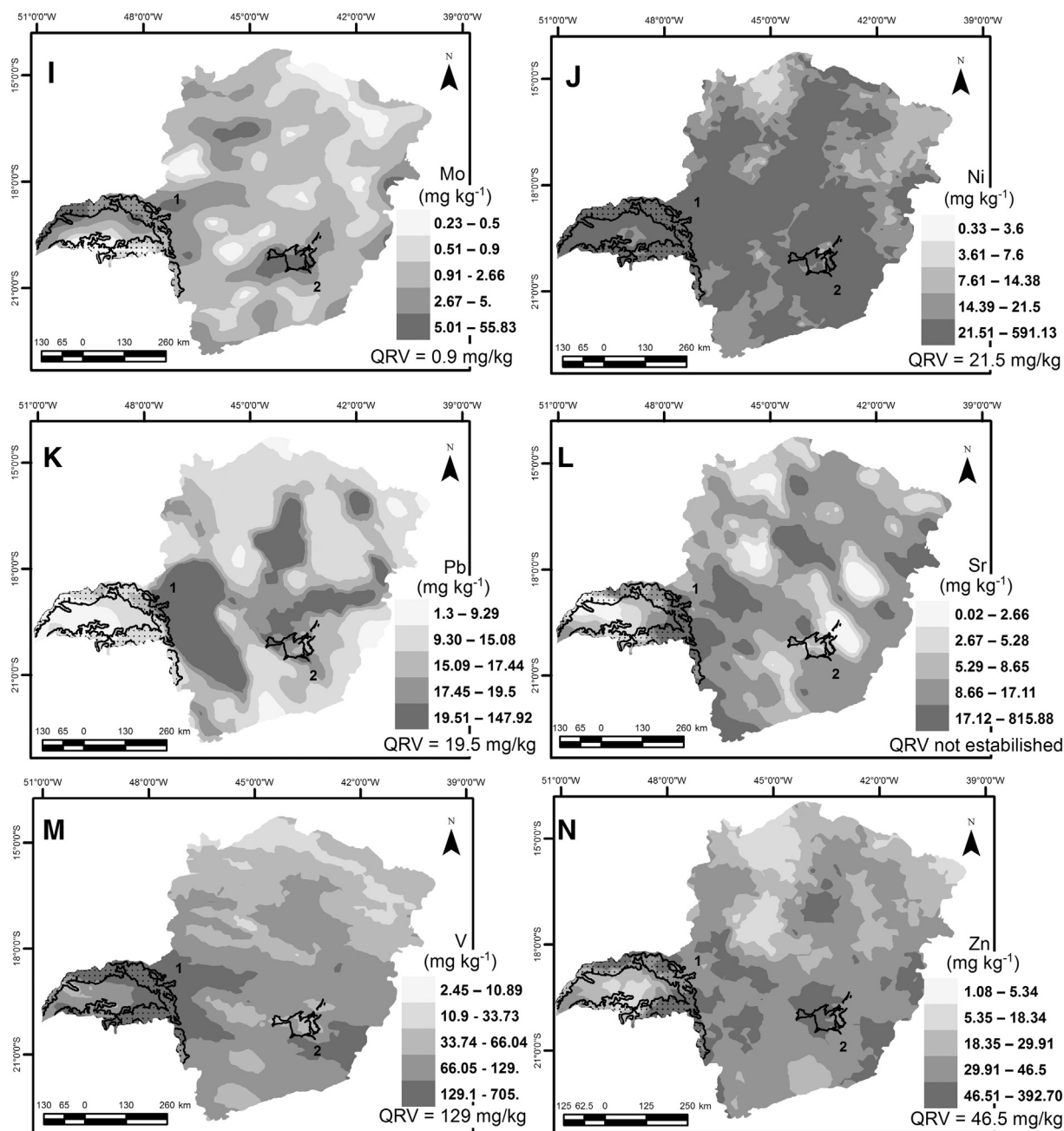


Fig. 5. Map of ordinary kriging of elements. Legend: 1 = Serra Geral Formation, 2 = Iron Quadrangle.

SOM and Fe concentration variables. This result highlights the importance of SOM in the maintenance of metal(loid)s in flooded and the virtually absence of Fe (hydr)oxides in these soils. On the other hand, Ferralsols showed an opposite behavior, suggesting a low affinity between organic matter and Fe (hydr)oxides in these soils. The weak correlation between SOM and Fe concentrations in soil groups which compose the second group supports this suggestion (Fig. 2).

The third group consists of incipient soils, Haplic Cambisols and Haplic Leptsols, which did not show high correlation values for relationships between metal(loid) concentrations and soil properties (Fig. 2). This result is attributed to early (incipient) stage of soil formation and high diversity of parent materials, suggesting that the metal(loid) concentrations of these soils are highly dependent on the nature of the parent material.

PCA aids the study of highly correlated variables (Wackernagel, 2003; McKillup and Dyar, 2010). As the metal(loid) concentrations and soil

properties are poorly correlated, the two- or three-dimensional plots, with the three first principal components, did not discriminate between the three groups of correlations (data not shown).

5.3. Spatial and cluster analysis

Higher metal(loid) concentrations relative to the Quality Reference Values of Minas Gerais were concentrated in two regions: i) the Iron Quadrangle, an area of 7200 km² known as the oldest mining area of Brazil and until today one of the most important areas of Au and Fe mining in the world (Schobbenhaus and Coelho, 1988; Dardenne and Schobbenhaus, 2001). This area comprises dominantly Archean gneiss and Proterozoic BIF, quartzite and schist; and ii) the Serra Geral Formation, the formal stratigraphic name for the mafic volcanic–plutonic igneous rocks, which covers Jurassic sandstones in the Paraná sedimentary basin. The Serra Geral Formation is dominated by the most fertile soils

Table 6

Descriptive statistics (mean - coefficient of variation (%)) of metal(loid) concentrations for the clusters.

Variable	Cluster			
	Granite-Gneiss Terrains	Clastic	Iron Quadrangle	Serra Geral
Al (g kg ⁻¹)	85.9–54 ^a	49.5–79 ^a	327–30 ^a	73.6–44 ^a
As (mg kg ⁻¹)	17.5–140	6.5–240	168–174 ^a	27.1–315
B (mg kg ⁻¹)	12.2–47 ^a	6.8–70 ^a	26.9–36 ^a	16.9–53 ^a
Ba (mg kg ⁻¹)	115–140	65.5–109	157–208	452–226 ^a
Cd (mg kg ⁻¹)	2.4–213	0.9–91	1.2–152	2.7–111
Co (mg kg ⁻¹)	11.3–113	5.3–115	8.8–147	51.9–50 ^a
Cr (mg kg ⁻¹)	146–76	61.4–81	61.9–92	480–135 ^a
Cu (mg kg ⁻¹)	60.4–53	23.8–67	28.9–166	189–48 ^a
Fe (g kg ⁻¹)	57.5–44 ^a	28.5–59 ^a	21.7–69 ^a	86.8–68 ^a
Hg (mg kg ⁻¹)	0.5–93	0.3–148	1.6–269 ^a	0.6–83
Mn (mg kg ⁻¹)	423–128	239–243	6301–197 ^a	1234–70
Mo (mg kg ⁻¹)	2.9–130	2.4–139	36.2–30 ^a	1.8–81
Ni (mg kg ⁻¹)	32.9–79	15.5–84	27.4–113	143–104 ^a
Pb (mg kg ⁻¹)	24.1–70 ^a	14.5–68	36.5–93	30.5–91
Sr (mg kg ⁻¹)	23.4–268 ^a	9.5–146	11.4–163	73.3–224 ^a
V (mg kg ⁻¹)	166–51	59.1–64	56.5–49	316–42
Zn (mg kg ⁻¹)	58.2–58 ^a	29.6–64 ^a	82.3–61 ^a	120–50 ^a
Cp (%)	45.7–41 ^a	31.5–67 ^a	17.1–52 ^a	54.6–21 ^a

^a Within the same variable, significantly different from means for all other clusters according to ANOVA following Tukey's HSD post-hoc test.

of Minas Gerais and constitutes the third largest contributor to the agricultural Gross National Product in Brazil (IBGE, 2013).

The Iron Quadrangle is the largest mineral province of Brazil, with deposits of Au, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pt and U (Dardenne and Schobbenhaus, 2001). The high concentration of metal(loid)s in soils of the Iron Quadrangle could be related to the presence of sulfides in gold bearing rocks and also to the presence of iron mineralization associated with the rocks from the Minas Supergroup in the region. Superposition of two main orogenic cycles, Transamazonian (Paleoproterozoic Era) and Brasiliano (Neoproterozoic Era), produced a variety of mineralogical assemblages in the more impure facies and multiple hydrothermal alteration events were responsible for mineralization of many metal(loid)s in host rocks of the Iron Quadrangle (Door, 1964; Pedrosa-Soares et al., 1994). Previous studies have already indicated that the Iron Quadrangle is an area with metal(loid) concentrations in soils above Quality Reference Values for soils in Minas Gerais (Deschamps et al., 2002).

The composition of mafic rocks from the Serra Geral Formation is typical of other continental flood basalts in the world (Rüegg, 1976; Peate, 1997); it contains phenocrysts occupying around 25% of the rock volume, trapped in volcanic glass. These phenocrysts are pyroxene, plagioclases, opaque crystals such as titanomagnetite or ilmenite, and occasionally some olivine (Romanini and Albuquerque, 2001). This mineral assemblage may be related to the high concentrations of metal(loid)s in the soils of the Serra Geral Formation (Romanini and Albuquerque, 2001; Oliveira and Costa, 2004).

The absence of abundant mineral parageneses in rocks of the Mantiqueira province relates to the lower metal(loid) concentrations than in soils in the Iron Quadrangle and the Serra Geral Formation (Peres et al., 2004). The dominance of gneiss in 70% of this area provides a relative geochemical homogeneity to the soils.

Although there is a lack of geochemical data on Neoproterozoic and Cretaceous sandstones of Minas Gerais, the absence of orebodies in these rocks suggests no metal(loid) mineralization (Pedrosa-Soares et al., 1994). Consequently, the soils derived from these rocks, with low Fe and clay concentrations, have the lowest metal(loid) concentrations.

Following the definition of the National Environment Council of Brazil (CONAMA, 2009), the Quality Reference Value for each state should represent its geological, climatic and geomorphological variability. In Minas Gerais, the percentage of the state with values above the Quality Reference Value and significant difference of the mean of metal(loid) concentrations among the clusters of soils expresses the variability of parent material and pedogenesis. Consequently, a single Quality Reference Value for each element does not represent the soil geochemical diversity.

6. Conclusions

The soils in the state of Minas Gerais reflect in general a weathered condition, with acidic pH, low concentrations of mobile elements and low values of cation exchange capacity. Higher concentrations of metal(loid)s are present than reported in previous studies of Brazilian soils. Metal(loid) concentrations in the soils of Minas Gerais are predominantly associated with particular parent materials, although a pedogenesis influence could be observed. The level of geochemical variability can be predicted to some extent by soil classification and mapping, which can be applied to define the number of samples required in future studies.

The correlation analysis suggests that the Fe concentrations are the main controlling agent for metal(loid) concentrations in the majority of soil groups in Minas Gerais, for soils with both low and high levels of iron when subjected to oxidizing conditions. Under anoxic conditions, the soil organic matter concentration increases in importance in the maintenance of metal(loid)s in soil.

The four clusters observed in the spatial distribution analysis were validated using appropriate statistical methods, indicating that just one Quality Reference Value from the whole state does not represent the soil geochemical diversity.

This work is the first effort to analyze the spatial distribution of metal(loid)s in Brazilian soils. The results obtained suggest that definition of Quality Reference Values in all states should be associated with geological provinces and dominant pedogenic processes.

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