Distribution and fractionation of the rare earth elements in Brazilian soils

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ABSTRACT

The distribution and fractionation of Sc, Y and 14 rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) were investigated in 144 samples (topsoil and subsoil) from 88 sites distributed across Brazil. Although, a wide range of natural variability in REE content was observed, overall the REE median contents were relatively low compared with those reported in soils from other parts of the world. The REE contents in Brazilian soils showed significant correlation mainly with Fe, Mn and Ti oxides, as well as organic matter. REE distribution in soils basically depend on the parent material, while fractionation of individual REEs depend on soil characteristics that are partly influenced by pedogenic process. Soils developed from alkaline igneous rocks showed the highest average content of REEs followed by sedimentary rocks, unconsolidated clay sediments, metamorphic rocks, basic igneous rocks, unconsolidated sand and silt sediments, and acid igneous rocks. REE normalized patterns varied significantly within each geological formation, except for soils derived from alkaline igneous rocks. The greatest variations were observed in the light REEs. Graphic inspection using exploratory data analysis tools such as Q–Q normal plots and boxplots was effective to recognize patterns and identify different data groups, determine threshold values and thus define the range of the background REE variability. The data set generated in this study may be used as a preliminary reference for regulatory actions in the Brazilian environmental legislation.

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1. Introduction

Natural contents of rare earth elements (REE) in soils are highly influenced by their parent materials, weathering state and pedogenetic processes, texture, and contents of organic matter and clay minerals (Hu et al., 2006). Furthermore, several studies have documented a gradual REEs increase in soils influenced by anthropogenic inputs (Aubert et al., 2004; Hu et al., 2006; Zhang and Shan, 2001). Industrial activities, agriculture and mining have been considered some of the major causes for the increase and redistribution of large quantities of these elements in soil.

In recent years, studies on trace elements including heavy metals, rare earth elements and radionuclides (Andersen et al., 2002; Doelsch et al., 2006; Li et al., 2008; Martin, 1997; Matschullat et al., 2012; Zhu and Shaw, 2000) have gained public attention because many illnesses have been associated with high concentrations of these elements in food and water due to soil pollution. The threat that these elements pose to human and animal health is aggravated by their long-term persistence in the environment. Studies conducted in areas with high REEs

concentrations reported that continuous exposure can cause damage to the circulatory, immunologic (Zhang et al., 2000), digestive (Zhang et al., 2000), respiratory (Censi et al., 2011), and nervous systems (He et al., 2008; Zhu et al., 2005), as well as decrease the intelligence quotient in children (Fan et al., 2004), and increase the risk of developing arteriosclerosis and pneumoconiosis (Sabbioni et al., 1982).

World resources of REEs are contained primarily in the minerals bastnäsite, monazite, loparite, and in ion-adsorption clays (U.S. Geological Survey, 2014). Bastnäsite deposits in alkaline rocks and carbonatites of China and the United States constitute the largest percentage of the world's economic resources, while monazite deposits in Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand, and the United States make up the second largest segment (Foley, 2013). Brazilian deposits account for about 1% of the world reserve (DNPM, 2010).

Currently, the use of REEs is closely associated with high-tech industry. The increasing use of REEs in industrial processes suggests that REE release into the environment is likely to increase in the future with potential impacts on human health (Sadeghi et al., 2013). Under this scenario, it is necessary to establish the natural REEs concentration in soil in order to monitor the impacts of human activity and understand the extent of the anthropogenic influence on the environment.

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Natural concentration of REEs in soils can be used to establish background levels, which allow identification of contaminated areas and contaminants in particular locations. These values are useful guidelines in studies of quantitative risk assessment and in the remediation, recycling and disposal of waste in soils (Gałuszka and Migaszewski, 2011). In Brazil, regional studies on the natural concentration of some trace elements in soils have been used to establish guideline values for environmental quality monitoring (Biondi, 2010; Caires, 2009; CETESB, 2001; Fadigas et al., 2002; Paye et al., 2010). However, there have been very few studies on REEs in Brazilian soils (Pérez et al., 1997), and no REE background level has yet been determined.

The goal of the present study is to determine the natural REEs distribution and fractionation in Brazilian soils at a national scale, investigate the relationship among elements distribution and soil properties, and establish natural backgrounds. Representative soil samples from different Brazilian regions were investigated.

2. Material and methods

2.1. Soil sample selection

Based on the natural occurrence of 11 soil orders and seven type of the rocks a total of 144 samples were selected from a soil bank (Minas Gerais Soil Bank/UFV) to represent the variability in soil types and lithotypes across the different geographic regions of Brazil (Fig. 1), and to ensure that the wide range of physical, chemical and mineralogical characteristics would be covered in the sample set. Selected soil samples were collected from 88 sites (Fig. 2) during field surveys carried out by researchers from the Universidade Federal de Viçosa (UFV) and Empresa Brasileira de Pesquisa Agropecuária (EMBRAPA). It was avoided selecting soil samples sampled from sites near urban environments and industries. The samples included 77 surface horizons (A-horizon) and 67 subsurface horizons (B or C-horizon). These samples were classified according to the Brazilian Soil Classification System (EMBRAPA, 2006) which is based on the World Reference Base for Soil Resources (IUSS, 2006). Surface horizons were defined here as topsoil samples and subsurface horizons as subsoil samples.

2.2. Sample preparation and characterization

All samples were air-dried, gently ground with the aid of a wooden rolling pin, manually homogenized in plastic bags, sieved through a 2.0 mm nylon mesh, and then stored in closed plastic containers. For REE analysis, a representative subsample of approximately 5 g of each soil sample was ground in an agate mortar to less than 0.125 mm mesh,
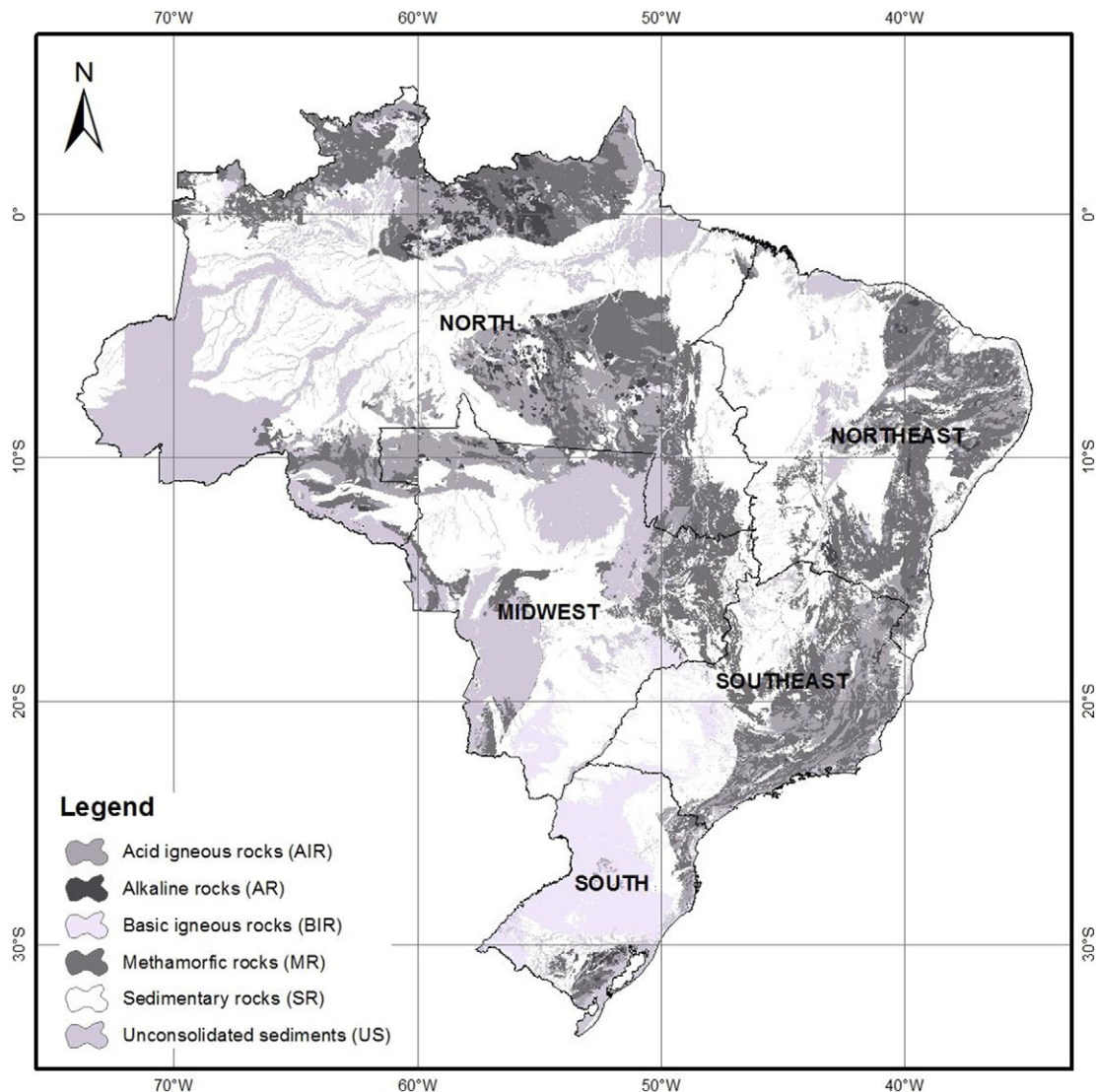

Fig. 1. Simplified lithotypes map at different geographic regions of Brazil.
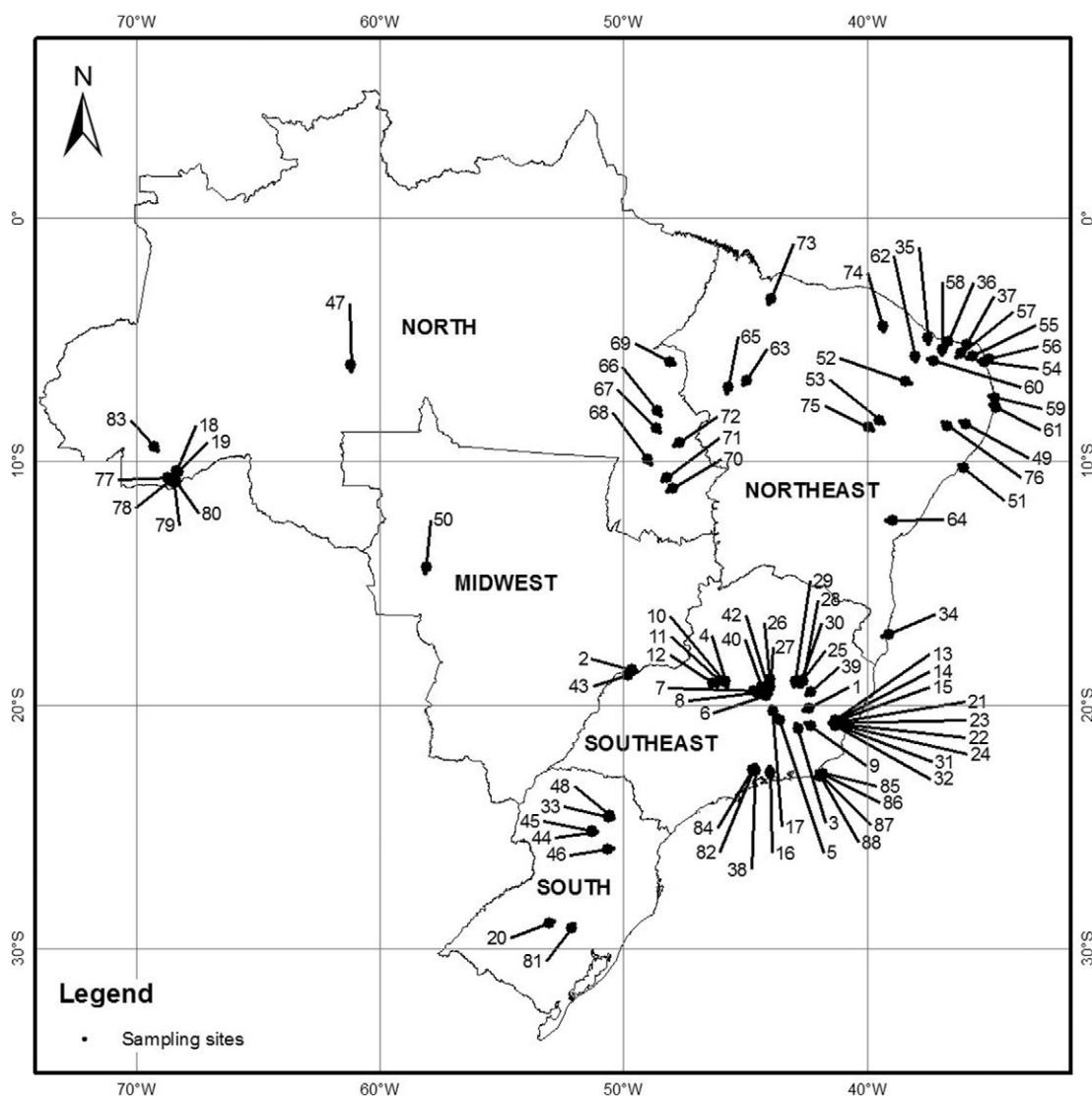
Fig. 2. Location of the sampling sites in the five Brazilian regions.

dried overnight in an electric oven at 80 °C, and stored in a desiccator until total digestion.

Physical and chemical properties of the soils were analyzed in the Geochemistry Laboratory at the UFV (Brazil), except for organic matter content, which was determined in the Geochemistry Laboratory of The University of Queensland (UQ, Australia). All soil property analyses were performed on air-dried soils sieved to less than 2 mm.

Soil pH was measured with a glass electrode in a 1:2.5 (v/v) soil:water ratio. Organic matter (OM) was determined by loss-on-ignition (LOI) at 430 °C for 16 h (Nelson and Sommers, 1996). Effective cation exchange capacity (CEC_{eff}) and soil weathering index (ki values) were measured according to the procedure described by EMBRAPA (1997). Non-crystalline Fe (Fe_{ox}) was determined by extraction with oxalic acid-buffered at pH 3.25 from a 1:50 (w/v) soil:solution mixture, under dark conditions as described in Pansu and Gautheyrou (2006). Crystalline plus non-crystalline Fe (Fe_d) were extracted with dithionite-citrate-bicarbonate, (1:25 w/v soil:solution ratio), as described by Pansu and Gautheyrou (2006). Crystalline Fe (Fe_{cr}) was obtained by the difference between Fe_d and Fe_{ox}. Oxides of Al, Mn and Ti were determined after extraction with 1:1 (v/v) 98% sulfuric acid:water ratio, according to the procedure described by EMBRAPA (1997). Iron, Al, Mn and Ti contents were determined by atomic absorption spectrophotometer AAS

(AA240FS, Varian, USA). Particle size was determined using the modified pipette method (Ruiz, 2005).

2.3. Sample digestion procedure

Total digestion was performed on a hotplate. Subsamples of 0.1000 g were placed in 50 mL Teflon® vessel sand pre-digested at 60 °C for 3 to 6 h with 3 mL of 1:1 (v/v) nitric acid:H_2O. Subsequently, 3 mL of hydrofluoric acid (40% HF) and 1 mL of nitric acid (70% HNO_3) were added. The vessels were capped and the suspension was refluxed at 120 °C for 24 h. Several times during this digestion step, the vessels were sonicated for 2 min in order to accelerate sample dissolution. Following acid digestion, the vessels were cooled to room temperature, opened, and the solutions were evaporated until near-dryness without boiling. If some solid residue remained at the bottom of the vessel, digestion was repeated (addition of 3 mL of 40% HF and 1 mL of 70% HNO_3) until a clear solution was obtained. Following this step, 1 mL of nitric acid (70% HNO_3) was added, and the vessels were capped, and refluxed overnight to near-dryness without boiling. This step was repeated three times. Finally, samples were diluted with 10 mL of 2% (v/v) nitric acid solution, transferred to 15 mL flasks and stored under refrigeration until analysis. Solutions were prepared using high purity reagents and ultrapure Milli-Q water (Milipore, Milford, MA).

Throughout the total digestion procedure, all Teflon® vessels, pipette tips and polypropylene bottles used for analyses were cleaned according to the procedures described by Gasparon (1998).

2.4. REEs determination

Rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) and Sc and Y concentrations were determined by inductively coupled plasma mass spectrometry (Thermo X7 ICP-MS). Samples preparation and analytical procedures were performed according to Eggins et al. (1997), except that Tm was not used as an internal standard. Certified samples W-2 and BIR-1 (U.S. Geological Survey Geochemical Reference Materials) were analyzed together with the soil samples at the beginning and the end of the run. The reference materials were also used for calibration purposes. Precision (as relative standard deviation) for the run, based on analyses of the duplicate extracts of W-2 and BIR-1 was ≤3% for all elements. The detection limits (DL), estimated according to Miller and Miller (1993) were ≤1.0 ng L^{-1} for all elements, except Sc (3.8 ng L^{-1}). All sample digestion steps and REEs analysis were carried out in the radiogenic isotope ultra-clean (Class 100) laboratory of the School of Earth Sciences, UQ.

2.5. Quality control

The quality of analytical procedures was checked using a procedural blank, a duplicate sample and a certified reference material-CRM (LKSD-2 from Canadian Certified Materials Project) for every batch of 24 soil samples. Reproducibility was evaluated by RSD for duplicates and CRM samples. Accuracy was determined by comparing the measured content with the certified value for CRM expressed as the percentage recovery (% R). Analyses of procedural blanks were lower than DL for all REEs. Satisfactory reproducibility (% RSD <8) was achieved for all elements in the CRM and duplicate sample. Accuracy of REEs for CRM varied between 90% (Tb) to 106% (Ce).

2.6. Statistical analysis

Descriptive statistical parameters such as average, median, minimum and maximum values, skewness, standard deviation (SDEV), median of the absolute deviations (MAD) and relative standard deviation (% RSD) were calculated from the geochemical dataset. Each soil property dataset was assessed in terms of median, minimum and maximum values. Crust-normalized REE patterns were used to evaluate REEs fractionation in topsoil and subsoil. Pearson's correlations analyses were performed to provide an overview on the relationships between REEs and chemical and physical soil properties. Assumptions on the geochemical data normality were evaluated using the Kolmogorov–Smirnov test (p ≤ 0.05). A square root-transformation for the geochemical data was applied in order to reduce asymmetry of the empirical distribution and to approximate a normal distribution model. Threshold values and REE background concentrations were determined by analyzing topsoil and subsoil data together. In this case, we opted for using bulk data (topsoil an subsoil sample together) because the data set thus obtained includes more samples and because the differences in REEs content between topsoil and subsoil samples were relatively small. Empirical cumulative probability normal plots (Q–Q normal plot) were used as a preliminary tool to identify multiple populations and geochemical data that lie outside the expected distribution range. Boxplot upper and lower inner fence of each square root-transformed uni-elemental data subset was used as the cut-off level for the outlier values, as well as to determine threshold values and define the background for REEs (Reimann et al., 2005). The upper inner fence and lower inner fence are defined, respectively, as: $\sqrt{xi} > \sqrt{(p75)} + 1.5\,(\sqrt{(p75)} - \sqrt{(p25)})$ and $\sqrt{x_i} < \sqrt{(p25)} - 1.5(\sqrt{(p75)} - \sqrt{(p25)})$ being x_i the outlier cut-off value, and p25 and p75 the 25th and 75th percentile of the distribution.

3. Results

3.1. Soil properties

The chemical and physical analyses revealed a wide variability of properties among the different soil samples (Table 1). Overall, topsoil and subsoil samples showed a relative enrichment in Fe, Mn and Al oxides, low CEC_{eff} and loamy-sandy particle size. On average, clay content was higher in subsoil samples. Soil pH_{H_2O} were almost similar in both sample types and, in general, was acidic. The average contents of organic matter were high (>4.5%) and predominantly higher in topsoil samples. Soil ki values (<2.2) indicated that most of the soil samples, both topsoil and subsoil, are highly weathered.

3.2. Distribution and fractionation of REEs in soils

Descriptive statistical parameters for Sc, Y and REEs content calculated for topsoil and subsoil are summarized in Table 2, together with the abundance of REEs in world soil (WS) (Bowen, 1979) and Upper Continental Crust (UCC) (Taylor and McLennan, 1995) for comparison.

The average content of REEs, Sc and Y was similar in topsoil and subsoil samples. The REE average content were slightly higher in subsoil compared to the topsoil samples, except for Eu (Table 2). This trend was also found for Sc and Y. Overall, the median REEs values in topsoil and subsoil samples were lower than those reported for the WS median (Bowen, 1979), whereas average values, solely for LREEs and Gd were higher than those reported by UCC (Taylor and McLennan, 1995). The average values also were higher than those reported by previous studies in Brazil (Pérez et al., 1997). Average content of Sc and Y in topsoil and

Table 1
Chemical and physical soil properties.

	pHH$_2$O	Fe$_{cr}$[a]	Fe$_{ox}$[b]	Al$_2$O$_3$	MnO	TiO$_2$	clay	OM[c]	Ki[d]	CECe$_{ff}$[e]
Topsoil		g kg^{-1}				%				cmol$_c$ dm^{-3}
Average	5.5	32.16	0.83	10.60	0.06	0.88	33	5.66	1.49	5.77
Median	5.2	22.52	0.62	10.63	0.02	0.48	31	4.24	1.46	3.08
Minimum	3.9	0.20	0.02	0.41	0.00	0.01	0	0.51	0.16	0.46
Maximum	8.3	144.24	3.26	34.59	0.70	4.97	80	27.09	3.04	56.05
Subsoil										
Average	5.3	40.31	0.74	12.42	0.06	0.77	39	4.86	1.43	3.90
Median	5.1	30.60	0.40	12.38	0.02	0.55	41	3.40	1.48	1.64
Minimum	4.3	0.00	0.02	0.69	0.00	0.05	4	0.28	0.18	0.25
Maximum	8.6	160.66	2.84	33.58	0.39	3.78	84	20.92	3.09	56.21

[a] Crystalline Fe.
[b] Non-crystalline Fe.
[c] Organic matter.
[d] Soil weathering index.
[e] efFective cation exchange capacity.

subsoil samples were lower than those reported for the WS median and by UCC. Only median Sc values in both soil samples were higher than those reported for the WS median. LREEs account for 93% of the total REE content determined in topsoil and subsoil, indicating that LREEs are more abundant in soils than heavy rare earth elements (HREEs: Gd to Lu), just as they are in the earth's crust (Laveuf and Cornu, 2009).

Soils that developed from alkaline igneous rocks showed the highest average content of REEs, followed by sedimentary rocks, unconsolidated clay sediments, metamorphic rocks, basic igneous rocks, unconsolidated sand and silt sediments, and acid igneous rocks (Fig. 3). With the exception of Tb, where the highest values were found in Luvissolos (Luvisols), the highest average REE contents were found in the Vertissolos (Vertisols) and Nitossolos (Nitosols) (Fig. 4) developed from sedimentary and metamorphic rocks, respectively, whereas the lowest REE content were found

in Plintossolos (Plinthosols), Planossolos (Planosols) and Espodossolos (Podzols) (Fig. 4) developed mostly from sandy sediments, metamorphic rocks and acid igneous rocks. These results are in agreement with findings from Earl-Goulet et al. (1997), Pérez et al. (1997) and Hu et al. (2006). In this study, REE abundances in soil types decreased, generally, in the following order: Vertissolos (Vertisols) > Nitossolos (Nitosols) > Cambissolos (Cambisols) > Latossolos (Ferralsols) > Neossolos (Arenosols and Leptosols) > Luvissolos (Luvisols) > Gleissolos (Gleysols) > Argissolos (Acrisols) > Plintossolos (Plinthosols) > Planossolos (Planosols) > Espodossolos (Podzols).

REE normalized patterns varied significantly within each geological formation, except for soils derived from alkaline igneous rocks (Fig. 5). In general, REE normalized patterns of topsoils and subsoils derived from these rocks are characterized by LREE enrichment (Fig. 5e and

Table 2
Descriptive statistical parameters for Sc, Y and rare earth elements (REEs) content in topsoil and subsoil samples together with the abundance these elements in world soil (WS) and Upper Continental Crust (UCC).

Element (mg kg⁻¹)	n[a]	Average	Median	Minimum	Maximum	Skewness	SDEV[b]	MAD[c]	% RSD[d]	WS median	UCC average
Sc										7.00	16.00
Topsoil	76	11.578	9.131	0.556	46.622	1.37	9.41	5.87	81.29		
Subsoil	67	12.816	9.974	0.724	53.397	1.61	10.08	5.42	78.69		
Y										40.00	24.00
Topsoil	77	17.834	13.808	0.027	67.786	1.16	13.11	7.28	73.52		
Subsoil	67	18.112	15.746	3.233	44.492	0.55	10.25	8.23	56.62		
La										40.00	30.00
Topsoil	77	38.084	29.998	0.103	197.631	1.93	35.75	18.02	93.87		
Subsoil	67	40.993	33.132	3.479	167.861	1.72	33.55	15.69	81.84		
Ce										50.00	64.00
Topsoil	77	87.129	69.745	0.228	418.759	2.06	80.64	39.01	92.55		
Subsoil	67	99.932	81.610	8.186	541.512	2.65	94.94	37.74	95.00		
Pr										7.00	7.10
Topsoil	77	8.157	6.442	0.022	38.812	1.67	7.27	4.42	89.11		
Subsoil	67	8.581	7.108	0.612	38.353	1.73	6.77	3.74	78.88		
Nd										35.00	26.00
Topsoil	77	27.340	22.999	0.077	114.427	1.52	23.75	13.78	86.88		
Subsoil	67	28.480	24.167	2.091	117.721	1.43	20.97	13.07	73.65		
Sm										4.50	4.50
Topsoil	77	5.225	4.474	0.013	21.601	1.25	4.24	2.65	81.21		
Subsoil	67	5.342	4.657	0.463	22.472	1.49	3.82	2.58	71.49		
Eu										1.00	0.88
Topsoil	77	1.050	0.631	0.002	6.372	2.44	1.21	0.46	114.91		
Subsoil	67	1.038	0.776	0.081	6.800	3.17	1.03	0.43	99.51		
Gd										4.00	3.80
Topsoil	77	3.929	3.448	0.008	15.841	1.26	3.08	1.83	78.49		
Subsoil	67	3.971	3.617	0.517	14.643	1.21	2.60	1.71	65.53		
Tb										0.70	0.64
Topsoil	77	0.600	0.515	0.001	2.227	1.11	0.44	0.29	73.25		
Subsoil	67	0.613	0.568	0.113	1.969	0.97	0.37	0.24	60.18		
Dy										5.00	3.50
Topsoil	77	3.337	2.752	0.005	12.010	1.05	2.39	1.56	71.76		
Subsoil	67	3.426	3.055	0.712	9.781	0.77	1.97	1.37	57.54		
Ho										0.60	0.80
Topsoil	77	0.651	0.526	0.001	2.334	1.04	0.47	0.28	71.77		
Subsoil	67	0.670	0.610	0.141	1.650	0.59	0.38	0.25	56.47		
Er										2.00	2.30
Topsoil	77	1.834	1.511	0.002	6.303	0.95	1.29	0.81	70.17		
Subsoil	67	1.902	1.584	0.427	4.201	0.54	1.06	0.81	55.82		
Tm										0.60	0.33
Topsoil	77	0.280	0.224	<0.001	0.891	0.84	0.19	0.11	68.59		
Subsoil	67	0.293	0.239	0.071	0.665	0.63	0.17	0.12	56.48		
Yb										3.00	2.20
Topsoil	77	1.807	1.462	0.002	5.630	0.86	1.21	0.70	66.75		
Subsoil	67	1.902	1.557	0.507	4.360	0.69	1.05	0.69	55.43		
Lu										0.40	0.32
Topsoil	77	0.274	0.215	<0.001	0.845	0.88	0.18	0.10	65.61		
Subsoil	67	0.290	0.229	0.082	0.682	0.77	0.16	0.10	55.07		

WS world soil from Bowen (1979); UCC upper continental crust from Taylor and Mclennan (1995).
[a] Number of samples.
[b] Standard deviation.
[c] Median of the absolute deviations.
[d] Relative standard deviation.

f) and a positive Eu anomaly. Only one topsoil and subsoil sample showed an anomalous pattern with relative enrichment in Tm, Yb and Lu.

In contrast, the REE normalized patterns of topsoils and subsoils derived from acid igneous rocks are characterized by a depletion in REEs, positive Ce and Sm anomalies, and a negative Eu anomaly (Fig. 5a and b). Only one subsoil sample shows a non-fractionated normalized pattern close to unity. The patterns of soils developed from basic igneous rocks are close to unity and either enriched or depleted in HREE, with either positive or negative Ce and Eu anomalies (Fig. 5c and d).

Soils developed from metamorphic rocks have very variable REE normalized patterns (Fig. 5g and h), with the majority of samples showing normalized values close to unity, a slight HREE depletion, and either positive or negative Eu anomalies. In contrast, sedimentary rocks and unconsolidated clay sediments show little or no LREE/HREE fractionation and normalized patterns close to unity. Some sample have a clear Ce positive anomaly, and subsoils are generally more depleted in HREE relative to topsoils (Fig. 5i to l). Normalized patterns of unconsolidated sands and silts are variable, with some samples close to unity, some showing significant REE depletion, and some LREE fractionation relative to HREE (Fig. 5m and n).
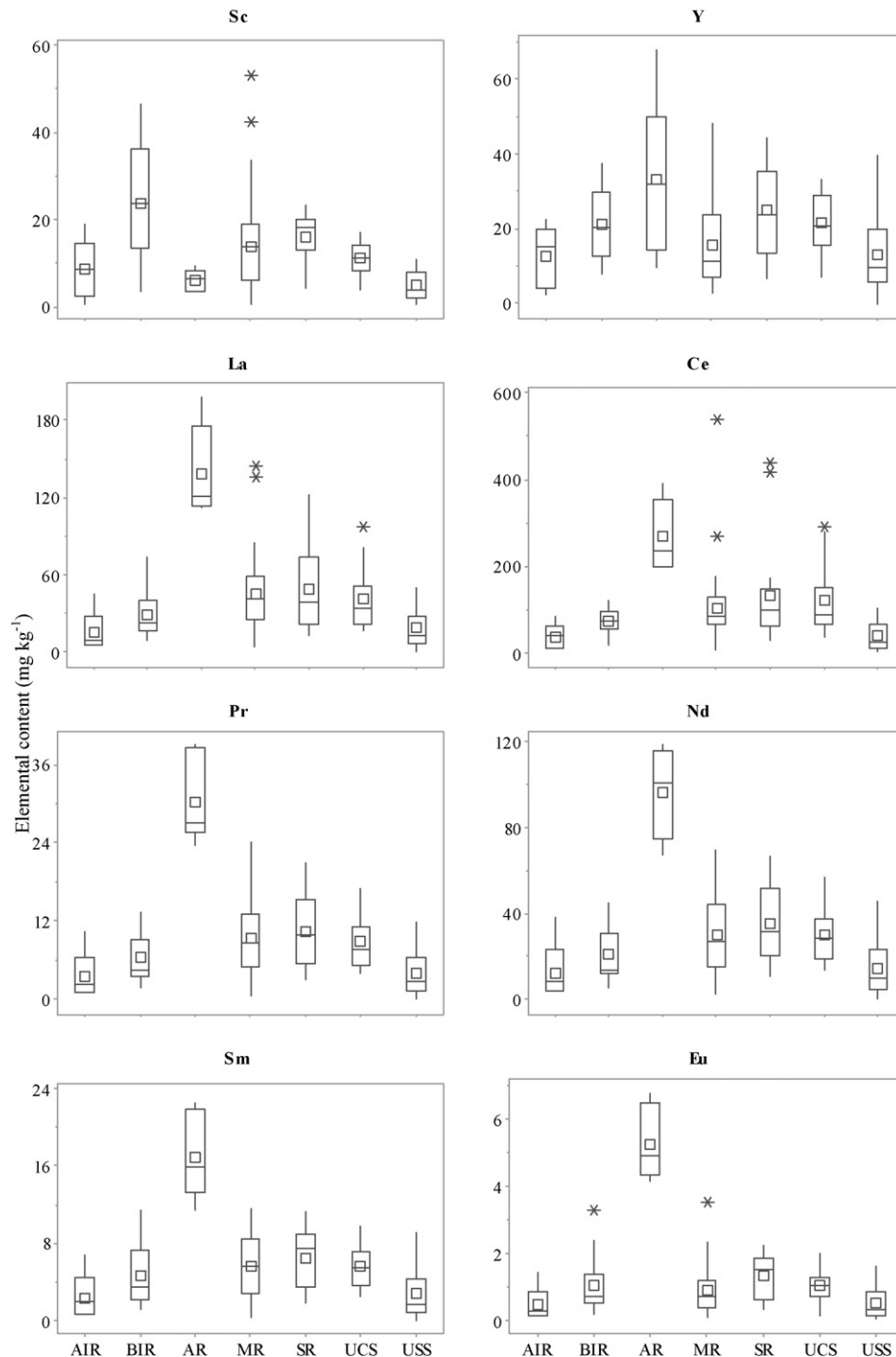

Fig. 3. Boxplots of Sc, Y and REEs in bulk sample (topsoil and subsoil samples) according to parent material. AIR acid igneous rocks (n = 5); BIR basic igneous rocks (n = 12); AR alkaline rocks (n = 6); MR metamorphic rocks (n = 52); SR sedimentary rocks (n = 19); UCS unconsolidated clay sediment (n = 14); USS unconsolidated sand and silt sediment (n = 36).

3.3. Correlation analysis

Tables 3 and 4 show the linear Pearson's correlation coefficients between soil properties (OM, clay, Fe_{cr}, Fe_{ox}, Al, Mn and Ti oxides, ki, pHH_2O and CEC_{eff}) and Sc, Y and REEs for topsoil and subsoil samples, respectively. The correlation analysis varied according to types of soil samples (topsoil e subsoil) and chemical element.

The Fe_{ox}, MnO and TiO_2 content in topsoil samples showed significant correlation with all elements analyzed (Table 3). Likewise, OM, Fe_{cr}, Al_2O_3, CEC_{eff}, clay and ki values showed significant correlation with most elements. However, soil pHH_2O showed few significant correlations.

For subsoil samples, only Fe_{ox} contents showed significant correlation with all elements, although Fe_{cr}, OM, TiO_2, clay, Al_2O_3 and CTC_{eff} correlated significantly with most of the elements (Table 4). The soil pH_{H2O} and MnO content showed significant correlations with some LREEs and Gd, and Sc, respectively. The ki values did not show significant correlations.

3.4. Data distribution patterns and outlier detection

The average values were higher than the median values, even as SDEV values were higher than the MAD for all REEs, indicating an asymmetric data distribution pattern for both topsoil and subsoil samples (Table 2). Moreover, the high positive skewness values suggest that
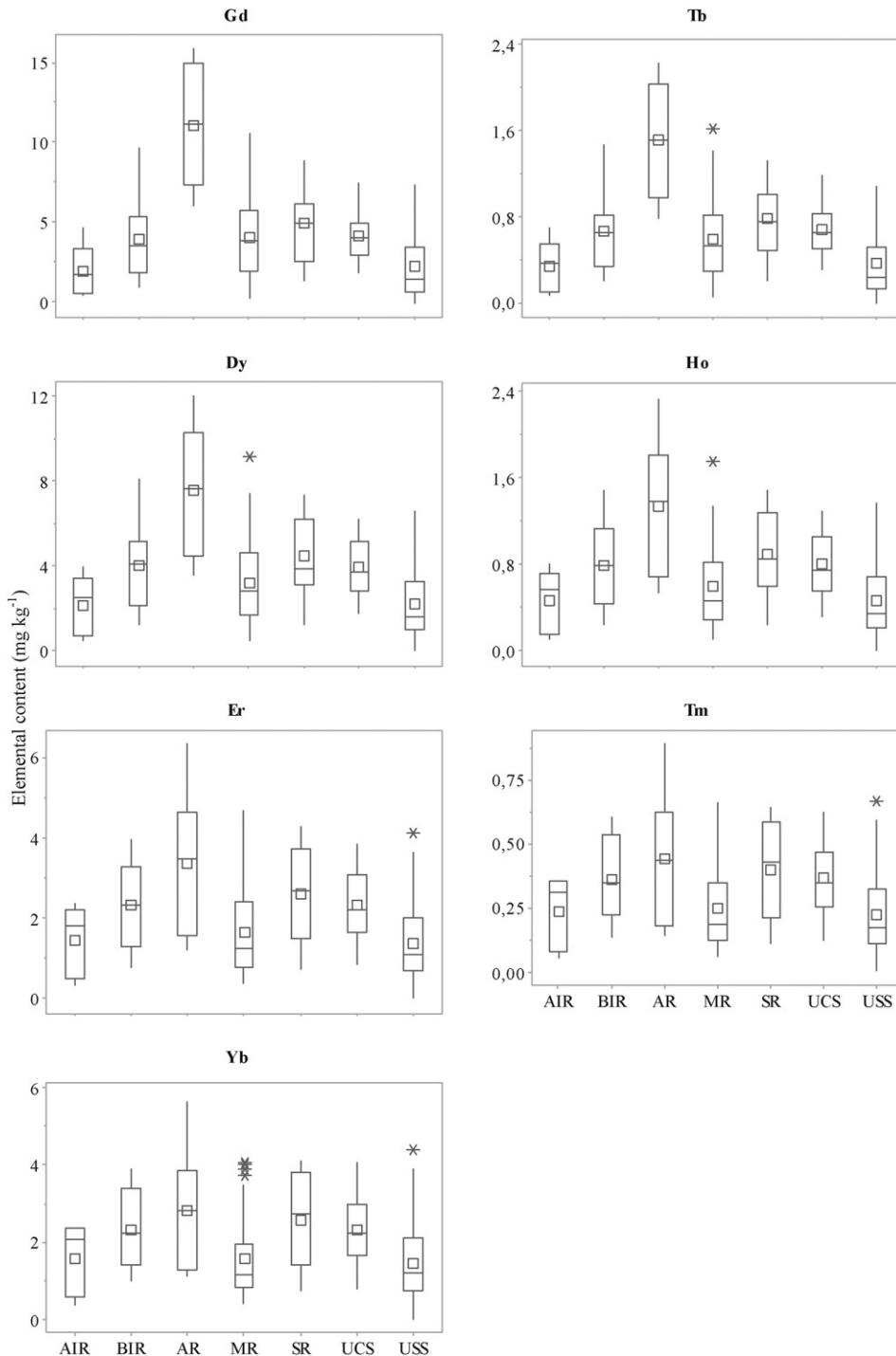

Fig. 3 (continued).

individual REE datasets were strongly right-skewed and that they did not follow a normal distribution model. According to the Kolmogorov–Smirnov test, none of the original variables showed a normal distribution ($p \leq 0.05$ for all REEs). The relative standard deviation (% RSD) values were high for all REE, particularly for LREEs (La to Eu) and Sc (Table 2).

The graphical inspection of original data distribution for all REEs in the Q–Q normal plot shows clear deviations from a normal distribution, with the possibility for at least two populations, together with some

obvious data outliers (data not shown). Boxplots detected 53 outlier values in the dataset, due to 16 anomalous soil samples (Table 5). Six of these samples derived from different soil orders (Cambissolos and Neossolos), but from the same parent material, namely alkaline rocks that have outlier values for all REEs except Sc (Table 5). Six anomalous samples of Latossolos and Cambissolos, derived from sedimentary rocks and unconsolidated clay sediments, have outlier values for La and Ce. Finally, two anomalous samples of Latossolos, derived from basic igneous rocks, and two samples of Latossolo and Argissolo derived
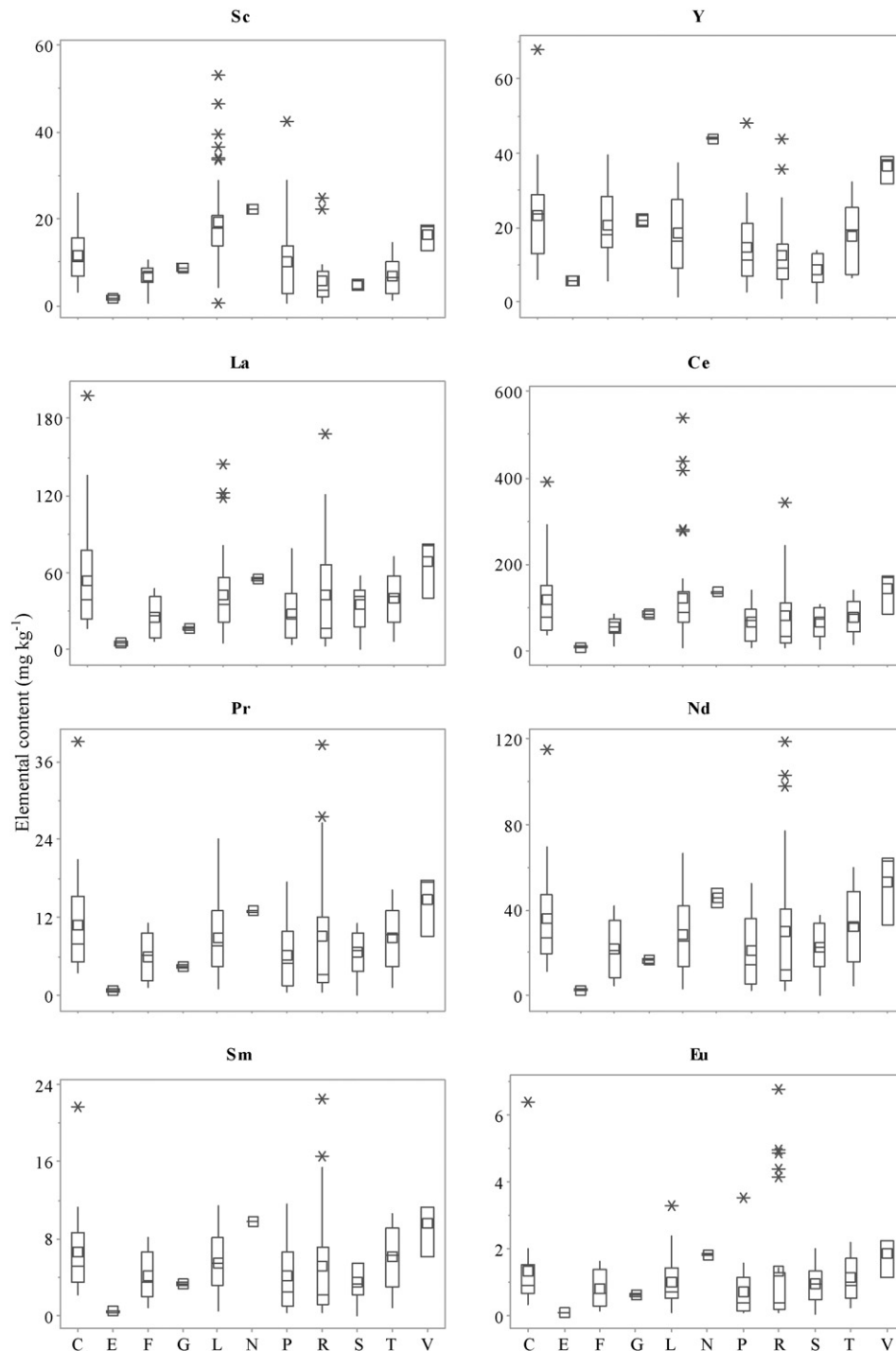

Fig. 4. Boxplots of Sc, Y and REEs in bulk sample (topsoil and subsoil) according to soil types. Soil type according to the Brazilian system of soil classification (EMBRAPA, 2006) and its equivalent in the World Reference Base for Soil Resources (IUSS, 2006) in brackets. C = Cambissolo (Cambisols); E = Espodossolo (Podzols); F = Plintossolo (Plinthosols); G = Gleissolo (Gleysols); L = Latossolo (Ferrosols); N = Nitossolo (Nitosols); P = Argissolo (Argisols); R = Neossolo (Arenosols and Leptosols); S = Planossolo (Planosols); T = Luvissolo (Luvisols); V = Vertissolo (Vertisols).

from metamorphic rocks, have outlier values for Sc and Eu, and Sc, La, Ce and Eu, respectively.

3.5. Background determination

After identifying and removing outlier data, a new data subset was prepared for background determination. The use of square root-transformation reduced the deviation between average and median, and SDEV and MAD of each uni-element data (Table 6), and had better symmetry compared to the respective raw data (Table 1). In addition, statistical test for normality showed that the square root-transformed uni-element data subsets were normally distributed for all REEs (p > 20),

except for Yb and Lu which do not strictly follow a normal distribution model. The boxplot of each square root-transformed uni-element data subset did not show any outlier value. Finally, threshold values were determined and the range of background variability for each REE was defined (Table 6).

4. Discussion

4.1. Soil properties

Brazil is characterized by a large diversity of soil types, resulting from the interaction of the different reliefs, climates, parent material,
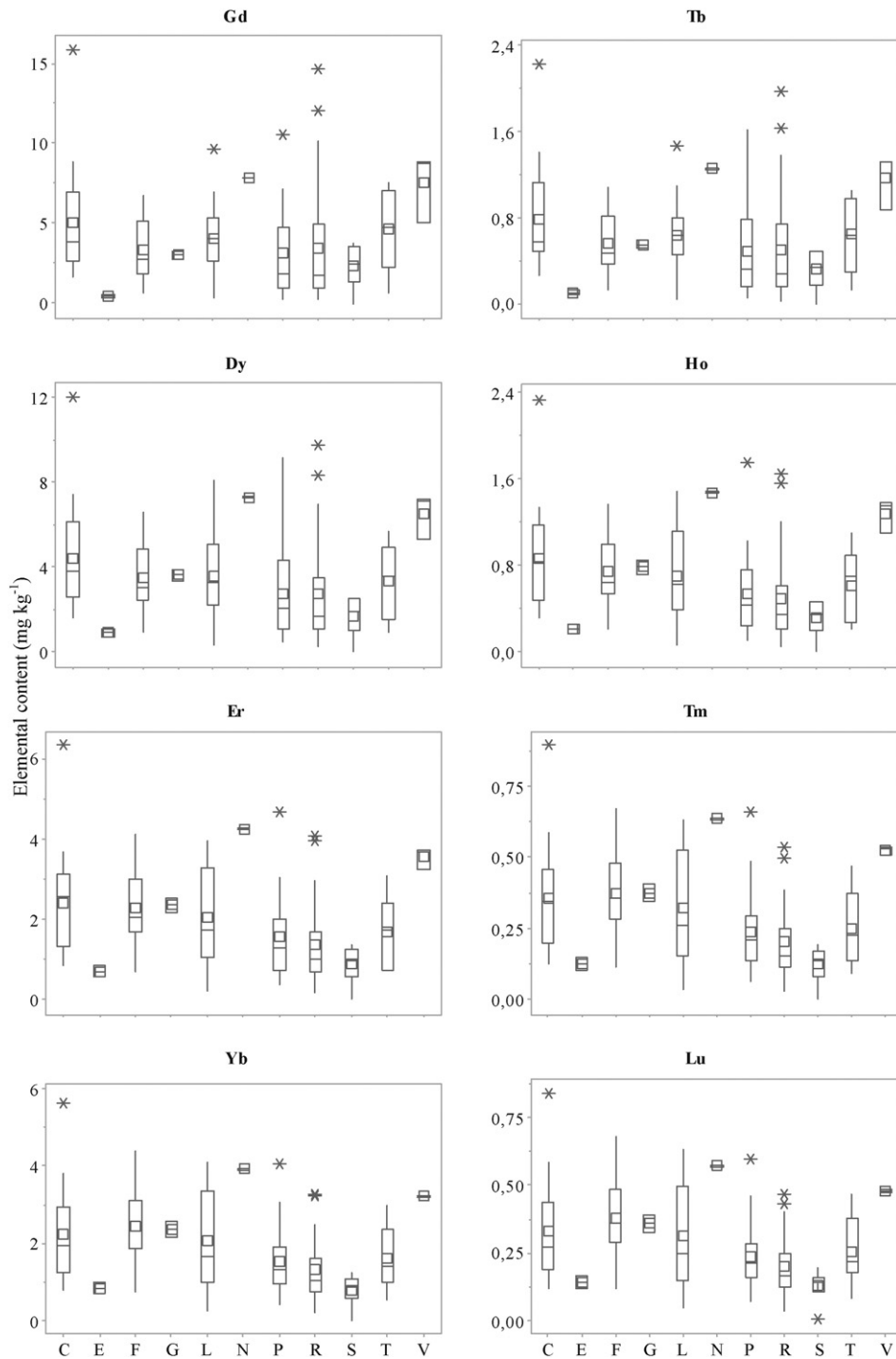

Fig. 4 (*continued*).

vegetation and associated organisms. The acidic character for most of the soil samples with relative enrichment in Fe, Mn, Al and Ti oxides and generally high weathering rates (ki values <2.2) reflect conditions typical of tropical soils. Effective cation exchange capacities are mostly low, and are related to depletion of major cations, mainly alkaline and alkaline earth elements. Soil texture is dominated by clay (with pre-dominance of kaolinite and iron oxides) and quartz-sand, with only minor amounts of silt. Similar characteristics were observed in previous studies in Brazilian soils (Matschullat et al., 2012; MINEROPAR, 2005;

Paye et al., 2010). According to Tyler (2004) these soil properties are important factors influencing adsorption, solubility, vertical transport and amount of REEs in soils.

4.2. Distribution and fractionation of REEs in soils

In our study, REE content varied significantly within and among the different parent materials due to soil formation factors. How a soil develops at a specific site depends on the relative importance of various
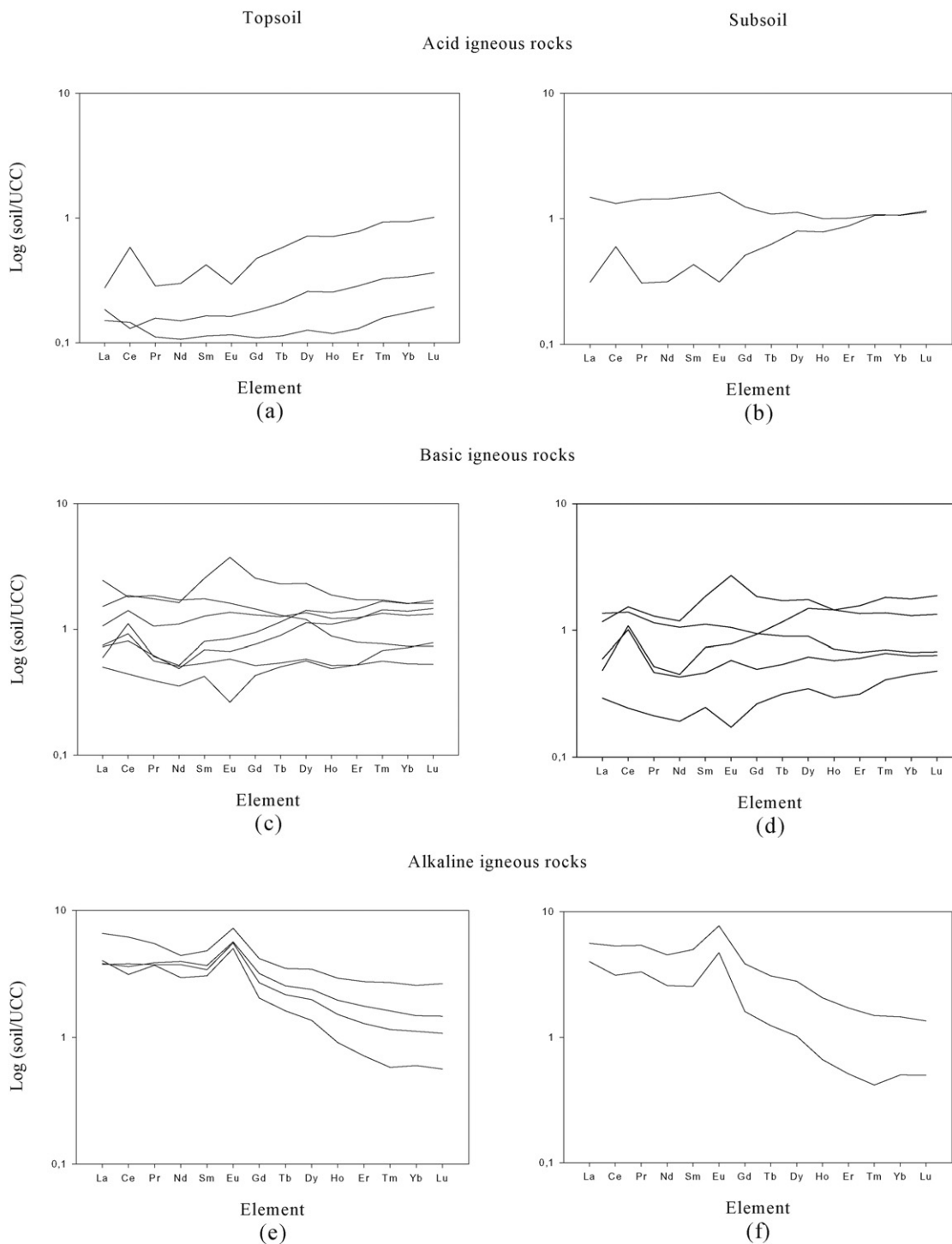

Fig. 5. Distribution of UCC-normalized REE patterns for topsoils and subsoils developed from acid (a–b), basic (c–d) and alkaline igneous rocks (e–f), metamorphic (g–h) and sedimentary rocks (i–j), unconsolidated clay sediment (k–l) and unconsolidated sand and silt sediments (m–n).
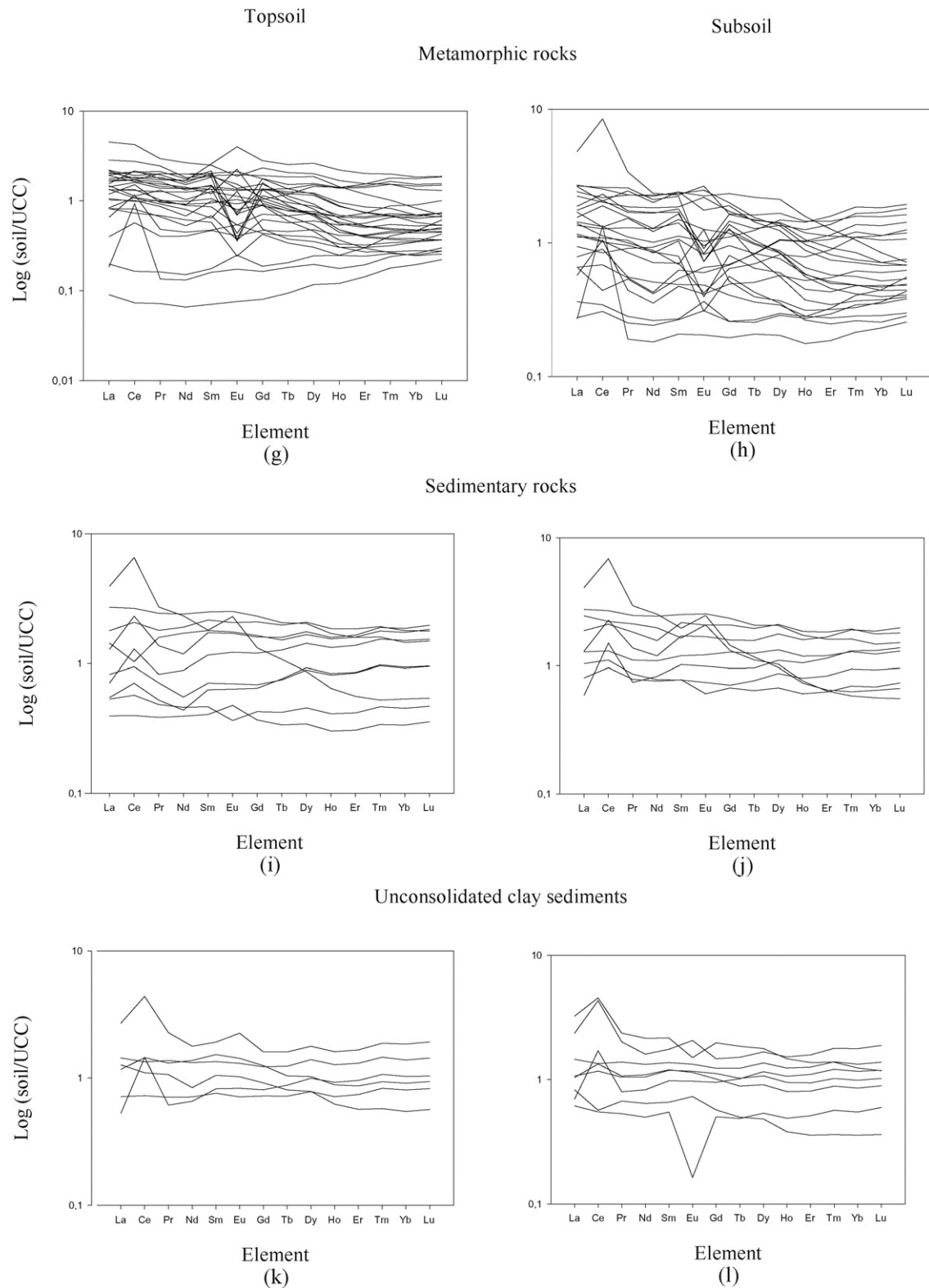
Topsoil

Subsoil

Metamorphic rocks

Element
(g)

Element
(h)

Sedimentary rocks

Element
(i)

Element
(j)

Unconsolidated clay sediments

Element
(k)

Element
(l)

Fig. 5 (*continued*).

soil-forming factors (i.e. climate, parent material, vegetation and fauna including man, topography, time). Furthermore, pedogenic processes may have fractionated and redistributed these elements through the weathering profile according to physical–chemical and biological processes resulting in depletion in some parts of the soil profile and enrichment in others (Laveuf and Cornu, 2009). However, the differences between average values for the topsoil and subsoil samples (topsoil/subsoil ratio) were relatively small. The high weathering stage of most of the samples (ki values <2.2), similar clay and oxide contents (mainly Mn), and little differences in the physical–chemical characteristics (low pH and CEC) between topsoil and subsoil samples were likely the main factors that influenced these results (Laveuf
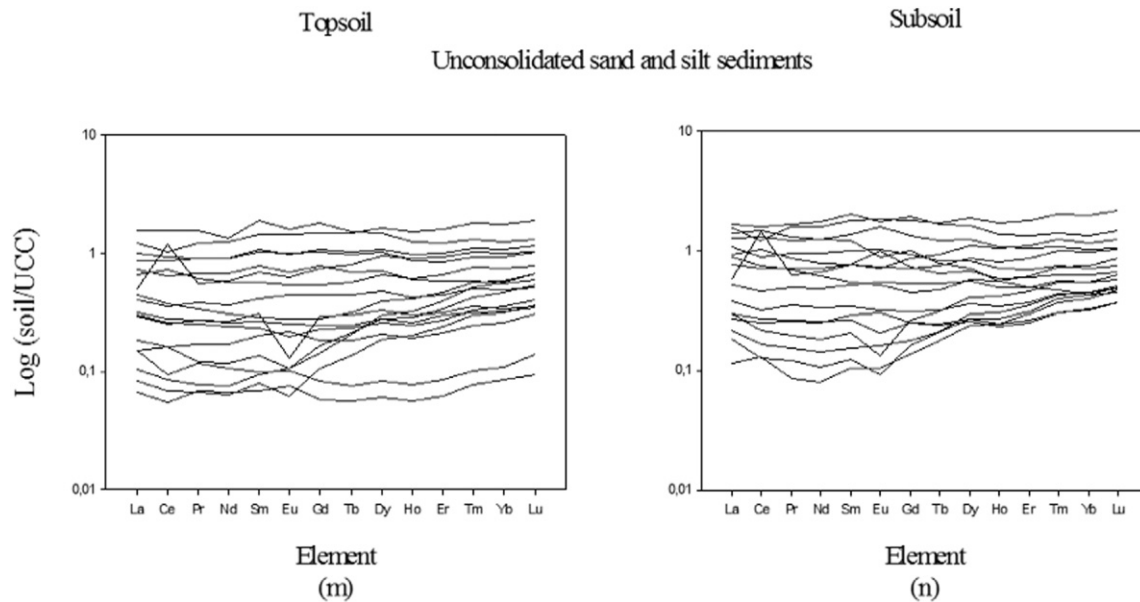
Topsoil   Subsoil

Unconsolidated sand and silt sediments

Fig. 5 (continued).

and Cornu, 2009; Middelburg et al., 1988; Minařík et al., 1998). In addition, is a indicative of soils do not disturbed by anthropogenic activities.

Parent material was a determinant factor for the distribution of REE contents, particularly for soils derived from alkaline rocks. Topsoils and subsoils derived from alkaline igneous rock (all the alkaline rocks considered in this study were nepheline-syenites) showed the highest REE contents and a enrichment of most REEs relative to UCC, independent on the type of soil, weathering degree and soil physical–chemical characteristics (Fig. 5e and f). These results may be explained by the mineralogical composition of the parent material, principally by the presence of accessory minerals rich in REEs and resistant to weathering (Clark, 1984). In contrast with alkaline rocks, basic igneous rocks are typically depleted in REEs. Thus, it could be expected that all soils derived from basic igneous rocks would show REE depletion relative to crustal abundances. However, the slight REE enrichment observed in some of the soil samples derived from basic igneous rocks (Fig. 5c and d) is due the characteristics of these soils (clayey and enriched in Fe and Mn oxides) that are different of the others. Thus, weathering of primary minerals in basalts releases REEs as well as Mn^{2+} and Fe^{2+} into the soil solution. These elements may be lost from the weathering

profile via the soil solution or can be incorporated, partially or totally, into secondary minerals and/or precipitate as oxides. REEs can accumulate in these secondary phases through one or a combination of the following mechanisms: coprecipitation, adsorption, surface complex formation, ion exchange, and penetration of the lattice (Laveuf and Cornu, 2009). In tropical soil conditions, coprecipitation with Fe and Mn oxides and adsorption in clay minerals are the most frequent REEs associations (Hu et al., 2006). Therefore, REEs associated with Mn and Fe oxides and clay minerals are not easily leached into solution, whereas silica and bases (Ca^{2+}, Mg^{2+}, K^+ and Na^+) are easily lost by leaching, resulting in a relative REE enrichment in soils derived from these rocks.

Acid igneous rocks are usually enriched in REEs compared with basic igneous rocks and, therefore, it can be expected that soils derived from these rocks are also relatively enriched in REEs. However, most of the soil samples derived from acid rocks did not show such REE enrichement (Fig. 5a and b). This is largely due to the fact that quartz is very resistant to weathering, and therefore may accumulate in soils and act as a REE diluent, as also observed for other trace elements (Hardy and Cornu, 2006). Moreover, if quartz remains in the soil, REEs may be easily removed from the surface and percolate through the soil profile, thus becoming more depleted in the topsoil and subsoil. In

Table 3
Correlation coefficient (r) between elemental content and soil properties in topsoil samples.

TOP	OM	Clay	Fe_{cr}	Fe_{ox}	Al_2O_3	MnO	TiO_2	Ki	pH	CTC_{eff}
Sc	0.60*	0.74*	0.94*	0.74*	0.76*	0.60*	0.80*	−0.09[NS]	0.21[NS]	0.40*
Y	0.38*	0.46*	0.37*	0.49*	0.37*	0.63*	0.42*	0.33*	0.20[NS]	0.38*
La	0.26[NS]	0.20[NS]	0.21[NS]	0.41*	0.21[NS]	0.48*	0.38*	0.27[NS]	0.26[NS]	0.27[NS]
Ce	0.35*	0.28[NS]	0.32*	0.37*	0.31*	0.41*	0.49*	0.06[NS]	0.18[NS]	0.19[NS]
Pr	0.31*	0.24[NS]	0.26[NS]	0.42*	0.24[NS]	0.56*	0.43*	0.31*	0.28*	0.32*
Nd	0.24[NS]	0.21[NS]	0.24[NS]	0.38*	0.19[NS]	0.57*	0.39*	0.37*	0.27[NS]	0.34*
Sm	0.35*	0.31*	0.38*	0.50*	0.29*	0.67*	0.51*	0.33*	0.31*	0.38*
Eu	0.33*	0.23[NS]	0.42*	0.44*	0.20[NS]	0.72*	0.62*	0.36*	0.31*	0.35*
Tb	0.39*	0.42*	0.44*	0.54*	0.35*	0.71*	0.54*	0.34*	0.27[NS]	0.42*
Gd	0.34*	0.34*	0.41*	0.52*	0.29*	0.72*	0.53*	0.36*	0.31*	0.42*
Dy	0.42*	0.47*	0.44*	0.54*	0.40*	0.68*	0.52*	0.31*	0.23[NS]	0.40*
Ho	0.43*	0.49*	0.43*	0.52*	0.42*	0.64*	0.48*	0.29*	0.19[NS]	0.38*
Er	0.43*	0.52*	0.40*	0.50*	0.44*	0.58*	0.44*	0.26[NS]	0.15[NS]	0.34*
Tm	0.44*	0.54*	0.38*	0.46*	0.46*	0.51*	0.39*	0.21[NS]	0.10[NS]	0.30*
Yb	0.44*	0.54*	0.37*	0.44*	0.46*	0.48*	0.38*	0.18[NS]	0.07[NS]	0.27[NS]
Lu	0.43*	0.53*	0.35*	0.41*	0.45*	0.45*	0.36*	0.17[NS]	0.06[NS]	0.26[NS]

*Significantly at level of $\alpha = 0.05$.
[NS], Not significant.

Table 4
Correlation coefficient (r) between elemental content and soil properties in subsoil samples.

SUB	OM	Clay	Fe$_{cr}$	Fe$_{ox}$	Al$_2$O$_3$	MnO	TiO$_2$	Ki	pH	CTC$_{eff}$
Sc	0.65*	0.61*	0.90*	0.65*	0.56*	0.30*	0.67*	−0.14[NS]	−0.08[NS]	0.08[NS]
Y	0.34*	0.47*	0.32*	0.42*	0.38*	0.21[NS]	0.23[NS]	0.09[NS]	0.22[NS]	0.33*
La	0.36*	0.22[NS]	0.36*	0.37*	0.17[NS]	0.22[NS]	0.43*	0.12[NS]	0.21[NS]	0.26[NS]
Ce	0.48*	0.31*	0.44*	0.41*	0.24[NS]	0.15[NS]	0.50*	−0.04[NS]	0.05[NS]	0.09[NS]
Pr	0.35*	0.23[NS]	0.35*	0.36*	0.19[NS]	0.21[NS]	0.41*	0.12[NS]	0.24[NS]	0.29*
Nd	0.23[NS]	0.18[NS]	0.26[NS]	0.29*	0.15[NS]	0.20[NS]	0.34*	0.20[NS]	0.30*	0.36*
Sm	0.28*	0.26[NS]	0.33*	0.34*	0.23[NS]	0.22[NS]	0.37*	0.15[NS]	0.29*	0.34*
Eu	0.26[NS]	0.26[NS]	0.38*	0.29*	0.20[NS]	0.21[NS]	0.53*	0.18[NS]	0.29*	0.32*
Tb	0.31*	0.40*	0.36*	0.40*	0.34*	0.25[NS]	0.37*	0.14[NS]	0.28*	0.36*
Gd	0.24[NS]	0.29*	0.31*	0.34*	0.25[NS]	0.23[NS]	0.35*	0.19[NS]	0.32*	0.38*
Dy	0.37*	0.47*	0.37*	0.43*	0.40*	0.24[NS]	0.36*	0.09[NS]	0.23[NS]	0.33*
Ho	0.40*	0.50*	0.36*	0.43*	0.43*	0.22[NS]	0.33*	0.05[NS]	0.20[NS]	0.31*
Er	0.42*	0.53*	0.35*	0.43*	0.46*	0.19[NS]	0.30*	0.00[NS]	0.15[NS]	0.26[NS]
Tm	0.45*	0.55*	0.34*	0.43*	0.48*	0.15[NS]	0.27[NS]	−0.05[NS]	0.10[NS]	0.22[NS]
Yb	0.46*	0.54*	0.33*	0.42*	0.48*	0.13[NS]	0.28[NS]	−0.07[NS]	0.08[NS]	0.19[NS]
Lu	0.45*	0.53*	0.30*	0.40*	0.46*	0.10[NS]	0.26[NS]	−0.08[NS]	0.07[NS]	0.18[NS]

*Significantly at level of $\alpha = 0.05$.
[NS], Not significant.

this case, the processes of leaching and erosion have a stronger control over REE distribution compared with relative enrichment due to weathering. These processes may have contributed significantly to REE depletion in most of topsoil and subsoil samples, especially LREE depeletion as LREEs are more easily mobile compared with HREEs during pedogenesis (Tyler, 2004).

UCC-normalized patterns of topsoil and subsoil samples developed from unconsolidated sand and silt sediments also suggest that the process of leaching and erosion predominates over the relative enrichment (Fig. 5m and n) by weathering of primary and secondary minerals. In this case, most of these soil samples show high amounts of quartz sand and low content of organic matter (<2%), Mn and Fe oxides, in addition to a high weathering degree (ki values <2.2 for all samples). Under such conditions, REEs released during weathering are not preserved in the soil through association with clay minerals and oxides. In contrast, the patterns of topsoil and subsoil samples derived from sedimentary rocks (Fig. 5i and j) and clay sediments (Fig. 5k and l) suggest a relative enrichment of REEs. Overall, these soil samples show high contents of clay, Fe and Mn oxides, as well as high values of pH and CEC. According to Tyler (2004) and Laveuf and Cornu (2009), these conditions favor REE retention in soils.

In general, the results obtained here show that the total content of REE in topsoil and subsoil samples basically depend on the mineralogy of the parent material, while the immobilization and fractionation of individual REEs depend on the soil characteristics (mainly texture, clay composition and physical–chemical characteristics) that are in turn influenced by pedogenic processes. This explains the variability in REE patterns of soils derived from the same parent material, and the apparently contradictory REE patterns described in the literature for geological samples derived from different kinds of igneous and metamorphic rocks. On the other hand, the most striking feature of the behavior of REE in samples derived from sedimentary materials, particularly coarse-grained materials, is the uniformity of the REE patterns. This indicates that the sedimentations process is very effective in homogenizing REE distribution irrespective of the parent material (Figueiredo, 1985).

The LREEs and HREEs anomalies in soils have been attributed to mineralogical composition and relative mineral stability in geogenic materials, as well as the properties of the different REEs in solution and association with secondary minerals (Laveuf and Cornu, 2009; Xing and Dudas, 1993). Therefore, it is probably the composition in primary minerals and the interaction between REEs and secondary minerals that accounts for differential mobilization of REE or group of REEs in soils. Soils derived from rocks rich in feldspars and plagioclases display a positive Eu anomaly, while micaceous soils can display either a positive or a negative Eu anomaly (Laveuf and Cornu, 2009). The same

comportment can happen for oxidic soils depending on soil pH (Cao, et al., 2001). According to Ma et al. (2002) amorphous or crystalline Fe and Mn oxides tend to retain up to 70% of total Ce in soils, and soils rich in these oxides may display a positive Ce-anomaly (Leybourne and Johannesson, 2008; Xing and Dudas, 1993).

4.3. Correlation study

Clay and organic matter content, Fe and Mn oxide content, pH and CEC are among the main soil properties influencing the content of REEs in soils (Hu et al., 2006). However, the influence of soil properties over the distribution of REEs may depend on the soil type, clay minerals, chemical element and pedogenetic processes (Tyler, 2004). According

Table 5
Descriptive statistical parameters of uni-element data outliers according to parent material.

Element (mg kg^{-1})	Outlier[a]	Average	Median	Minimum	Maximum
Alkaline rocks					
Y	1	67.785	67.785	67.785	67.785
La	4	151.548	144.177	120.210	197.630
Ce	4	283.645	270.986	199.278	393.330
Pr	4	31.731	32.276	23.563	38.811
Nd	6	95.920	99.938	66.993	117.721
Sm	4	17.307	17.661	11.436	22.471
Eu	6	5.260	4.917	4.159	6.800
Gd	2	15.242	15.242	14.642	15.841
Tb	1	2.226	2.226	2.226	2.226
Dy	1	12.010	12.010	12.010	12.010
Ho	1	2.333	2.333	2.333	2.333
Er	1	6.303	6.303	6.303	6.303
Tm	1	0.890	0.890	0.890	0.890
Yb	1	5.630	5.630	5.630	5.630
Lu	1	0.844	0.844	0.844	0.844
Basic igneous rocks					
Sc	1	46.622	46.622	46.622	46.622
Eu	1	3.284	3.284	3.284	3.284
Metamorphic rocks					
Sc	2	47.977	47.977	42.558	53.397
La	2	139.905	139.905	135.130	144.680
Ce	2	405.607	405.607	269.702	541.511
Eu	1	3.512	3.512	3.512	3.512
Sedimentary rocks					
La	1	122.105	122.105	122.105	122.105
Ce	2	428.766	428.766	418.759	438.773
Unconsolidated clay sediment					
Ce	3	282.072	279.483	276.297	290.435

[a] Number of outlier values.

Table 6
Descriptive statistical parameters of square root-transformed uni-element data subset.

Element (mg kg^{-1})	Average $\sqrt{x}$	Median $\sqrt{x}$	MAD[a] $\sqrt{x}$	SDEV[b] $\sqrt{x}$	Skewness $\sqrt{x}$	Threshold values $\sqrt{x}$	Background range $(\sqrt{x})^2$
Sc	3.135	3.065	0.98	1.26	0.12	0.745–6.310	0.555–39.816
Y	3.971	3.880	1.13	1.36	0.03	0.163–6.933	0.027–48.066
La	5.420	5.544	1.49	2.18	0.18	0.321–10.867	0.103–118.092
Ce	8.016	8.340	1.98	3.03	−0.22	0.477–15.588	0.228–175.748
Pr	2.562	2.548	0.77	1.06	0.13	0.149–5.239	0.022–24.030
Nd	4.639	4.696	1.37	1.85	−0.08	0.278–8.308	0.077–69.023
Sm	2.065	2.113	0.66	0.82	−0.06	0.112–4.064	0.013–11.601
Eu	0.838	0.805	0.27	0.35	0.12	0.040–1.544	0.002–2.384
Gd	1.822	1.873	0.50	0.69	−0.06	0.091–3.475	0.008–10.602
Tb	0.726	0.730	0.17	0.26	−0.03	0.033–1.403	0.001–1.621
Dy	1.722	1.723	0.46	0.60	−0.03	0.071–3.127	0.005–9.145
Ho	0.762	0.750	0.20	0.26	0.01	0.030–1.327	0.001–1.761
Er	1.285	1.238	0.35	0.43	0.03	0.049–2.154	0.002–4.640
Tm	0.505	0.479	0.12	0.17	0.08	0.018–0.816	<0.001–0.666
Yb	1.296	1.230	0.30	0.40	0.26	0.432–2.088	0.187–4.360
Lu	0.506	0.469	0.11	0.15	0.31	0.174–0.826	0.030–0.682

[a] Median of the absolute deviations.
[b] Standard deviation.

to Peng and Wang (1995) it is common for these factors to be partly associated with physical and chemical differences among soil horizons, and to reflect variations in geochemical behavior and distribution of REEs.

In the current investigation, contents of Fe, Mn and Ti oxides, as well as organic matter were the main variables significantly correlated with the contents of REEs in topsoil (Table 3). The same correlations, with the exception of Mn content, were observed in subsoil samples (Table 4). This suggests that Mn oxides have little influence on the amounts of REEs at depth, and that other clay minerals have a stronger control on REE distribution in this horizon. This result corroborates Palumbo et al. (2001) studies on the affinity of REEs to oxides, where it was reported that Fe, Al and Mn (hydr) oxides can co-precipitate, adsorb and incorporate various REEs in their structure, in amounts varying with type (Wang et al., 2001), depth (Yan et al., 1999) and soil pH (Hu et al., 2006), and sometimes without correlation with Fe and Mn contents (Yan et al., 1999). Organic matter can also retain significant amounts of REEs, because it can complex, adsorb or chelate positively charged REEs in amounts varying with the type, composition and content of OM, soil pH and redox conditions (Pourret et al., 2007). The adsorption of REEs increases with increasing soil pH and CEC values because the surface of soil particles charged with OH$^-$ increases as the soil pH increases, thus increasing CEC values. In addition, CEC is mainly affected by the content and composition of clay, organic matter, and weathering intensity of soils. Although the weathering index (ki values) did not show significant correlation coefficients with most REEs in topsoil samples, the REE pattern distributions (Fig. 5) already indicated that the mobilization/immobilization of individual REEs in this horizon are affected by weathering and leaching intensity. Similar results were obtained by Minarik et al. (1998) and Middelburg et al. (1988) in their studies of REE distribution during soil development processes.

4.4. Outlier detection and background determination

According to Reimann et al. (2005) outlier values must be removed, especially if they can be grouped in a separate population, because they result in changes of estimates of the descriptive statistics and may potentially affect the asymmetry of the empirical distribution of the elemental dataset. Therefore, the threshold values and the background range were defined separately for these values (Table 6). The concept of transforming data in order to reduce asymmetry of an empirical density distribution has been widely suggested in geochemical data analysis (Campell, 1982; Sinclair, 1983). Log-transformation of data is the most common numerical transformation used for geochemical or environmental dataset (Reimann and Filzmoser, 2000). However, in this study, the square root-transformed uni-elemental data subset better adjusted to the normal distribution compared to the log-transformation (data not shown). The REEs data obtained in this study for topsoil and subsoil is the first set of reference data for REEs distribution in Brazilian soils. The data did not show evidence of anthropogenic influence at any of the selected sites, demonstrating that the site selection was suitable for the establishment of reliable natural background data at non-contaminated sites. It is therefore recommended that threshold values and the range of the background variability determined in this work be adopted as a preliminary regulatory reference for REEs in Brazilian soils.

5. Conclusions

The average and median values for REE concentrations in Brazilian topsoils and subsoils were lower than the world median and higher than the average values reported by previous studies in Brazil. Nevertheless, REE concentrations are overall similar to those reported for the Upper Continental Crust.

Total REE contents in topsoils and subsoils basically depend on the parent material, while fractionation of individual REEs depend on soil characteristics that are partly influenced by pedogenic process.

LREEs are more abundant than HREEs in both topsoils and subsoils, and the distribution patterns of UCC-normalized REE contents show, in general, significant LREE depletion.

Iron, Mn and Ti oxides, as well as organic matter were the main variables significantly correlated with REE contents.

Cumulative probability normal (Q–Q Normal) plots and boxplots are a powerful tool to discriminate different populations of samples, detect outliers, and determine REEs threshold values and thus define their range of background variability.

References

Andersen, M.K., Raulund Rasmussen, K., Hansen, H.C.B., Strobel, B.W., 2002. Distribution and fractionation of heavy metals in pairs of arable and afforested soils in Denmark. Eur. J. Soil Sci. 53, 491–502.

Aubert, D., Probst, A., Stille, P., 2004. Distribution and origin of major and trace elements (particularly REE, U and Th) into labile and residual phases in an acid soil profile (Vosges Mountains, France). J. Appl. Geochem. 19, 899–916.

Biondi, C.M., 2010. Background Concentrations of Heavy Metalsin Benchmark Soils of Pernambuco State, Brazil. 2010 Thesis, UFRP, Recife (58 pp. (in Portuguese with English abstract)).

Bowen, H.J.M., 1979. Environmental Chemistry of the Elements. Academic Press, London (333 pp.).

Caires, S.M., 2009. Determination of Natural Heavy Metals Levels in Soils of Minas Gerais State to Help Definition of Background Levels. 2009 PhD thesis, UFV, Viçosa (304 pp. (in Portuguese with English abstract)).

Campell, N.A., 1982. Statistical treatment of geochemical data. In: Smith, R.E. (Ed.), Geochemical Exploration in Deeply Weathered Terrain. CSIRO Institute of Energy and Earth Resources, Floreat Park, W.A., pp. 141–144.

Cao, X., Chen, Y., Wang, X., Deng, X., 2001. Effects of redox potential and pH value on the release of rare earth elements from soil. Chemosphere 44, 655–661.

Censi, P., Tamburo, E., Speziale, S., Zuddas, P., Randazzo, L.A., Punturo, R., Cuttitta, A., Aricò, P., 2011. Yttrium and lanthanides in human lung fluids, probing the exposure to atmospheric fallout. J. Hazard. Mater. 186, 1103–1110.

CETESB — Companhia De Tecnologia De Saneamento Ambiental. 2003, 2001. Relatório de estabelecimento de valores orientadores para solos e água subterrâneas no Estado de São Paulo. CETESB, São Paulo (247 pp. (in Portuguese)).

Clark, A.M., 1984. Mineralogy of the rare earth elements. In: Henderson, P. (Ed.), Rare Earth Element Geochemistry. Elsevier Science, New York, pp. 33–54.

DNPM — Departamento Nacional De Produção Mineral, 2010. Terras raras. http://www.dnpm.gov.br/assets/galeriadocumento/sumariomineral2004/TERRAS%20RARAS%202004.pdf (last search 03.05.2013).

Doelsch, E., Van De Kerchove, V., Saint Macary, H., 2006. Heavy metal content in soils of Réunion (Indian Ocean). Geoderma 134, 119–134.

Earl-Goulet, J.R., Mahaney, W.C., Hancock, R.G.V., Milner, M.W., 1997. Geochemistry of spodosols formed in holocene till, Norra Storfjället Massif, northern Sweden. J. Radioanal. Nucl. Chem. 219, 7–17.

Eggins, S.M., Woodhead, J.D., Kinsley, L.P.J., Mortimer, G.E., Sylvester, P., McCulloch, M.T., Hergt, J.M., Handler, M.R., 1997. A simple method for the precise determination of ≥40 trace elements in geological samples by ICPMS using enriched isotope internal standardisation. Chem. Geol. 134, 311–326.

Empresa Brasileira De Pesquisa Agropecuária — Embrapa, 1997. Manual de métodos de análises de solos 2nd ed. Centro Nacional de Pesquisa de Solos, Rio de Janeiro (212 pp.).

Empresa Brasileira De Pesquisa Agropecuária — Embrapa, 2006. Sistema Brasileiro de Classificação de Solos 2nd ed. Embrapa Informação Tecnológica, Brasília (306 pp.).

Fadigas, F.S., Sobrinho, N.M.B.A., Mazur, N., Anjos, L.H.C., Freixo, A.A., 2002. Concentrações naturais de elementos traço em algumas classes de solos brasileiros. Bragantia 61, 151–159 (in Portuguese with English abstract).

Fan, G., Yuan, Z., Zheng, H., Liu, Z., 2004. Study on the effects of exposure to rare earth elements and health-responses in children aged 7–10 years. Wei Sheng Yan Jiu 33, 23–28.

Figueiredo, M.C.H., 1985. Introdução à geoquímica dos elementos terras raras. Boletim IG-USP 16 pp. 15–31.

Foley, N.K., 2013. Rare earth elements: the role of geology, exploration, and analytical geochemistry in ensuring diverse sources of supply and a globally sustainable resource. J. Geochem. Explor. 133, 1–5.

Gałuszka, A., Migaszewski, Z., 2011. Geochemical background — an environmental perspective. Mineralogia 42, 7–17.

Gasparon, M., 1998. Trace metals in water samples: minimising contamination during sampling and storage. Environ. Geol. 36, 207–214.

Hardy, M., Cornu, S., 2006. Location of natural trace elements in silty soils using particle-size fractionation. Geoderma 133, 295–308.

He, X., Zhang, Z., Zhang, H., Zhao, Y., Chai, Z., 2008. Neurotoxicological evaluation of long-term lanthanum chloride exposure in rats. Toxicol. Sci. 103, 354–361.

Hu, Z., Haneklaus, S., Sparovek, G., Schnug, E., 2006. Rare earth elements in soils. Commun. Soil Sci. Plant Anal. 37, 1381–1420.

Iuss, 2006. World reference base for soil resources. World Soil Resources Reports, 103. FAO, Rome (145 pp.).

Laveuf, C., Cornu, S., 2009. A review on the potentiality of rare earth elements to trace pedogenetic processes. Geoderma 154, 1–12.

Leybourne, M.I., Johannesson, K.H., 2008. Rare earth elements (REE) and yttrium in stream waters, stream sediments, and Fe–Mn oxyhydroxides: fractionation, speciation, and controls over REE + Y patterns in the surface environment. Geochim. Cosmochim. Acta 72, 5962–5983.

Li, C., Kang, S., Wang, X., Ajmone-Marsan, F., Zhang, Q., 2008. Heavy metals and rare earth elements (REEs) in soil from the Nam Co Basin. Tibetan Plateau. Environ. Geol. 53, 1433–1440.

Ma, Y.-J., Huo, R.-K., Liu, C.-Q., 2002. Speciation and fractionation of rare earth elements in a lateritic profile from southern China: identification of the carriers of Ce anomalies. Proceedings of the Goldschmidt Conference, Davos, Switzerland.

Martin, C.W., 1997. Heavy metal concentrations in floodplain surface soils, Lahn River, Germany. Environ. Geol. 30, 119–125.

Matschullat, J., Höfle, S., Da Silva, J., Mello, J., Melo, G., Pleßow, A., Reimann, C., 2012. A soil geochemical background for northeastern Brazil. Geochem. Explor. Environ. Anal. 12, 197–209.

Middelburg, J.J., Van Der Weijden, C.H., Woittiez, J.R.W., 1988. Chemical processes affecting the mobility of major, minor and trace elements during weathering of granitic rocks. Chem. Geol. 68, 253–273.

Miller, J., Miller, J., 1993. Statistics for Analytical Chemistry. 3rd ed. Ellis-Horwood, London (233 pp.).

Minařík, L., Žigová, A., Bendl, J., Skřivan, P., Šťastný, M., 1998. The behaviour of rare-earth elements and Y during the rock weathering and soil formation in the Říčany granite massif, Central Bohemia. Sci. Total Environ. 215, 101–111.

Mineropar, 2005. Minerais do Paraná S. A. Geoquímica de solo — Horizonte B. Levantamento Geoquímico Multielementar do Estado do Paraná vol. 2. Mineropar, Curitiba (407 pp. (in Portuguese)).

Nelson, D.W., Sommers, L.E., 1996. Total carbon, organic carbon, and organic matter. In: Page, A.L., et al. (Eds.), Methods of Soil Analysis, Part 2, 2nd ed. Agronomy 9. Am. Soc. of Agron., Inc., Madison, WI, pp. 961–1010.

Palumbo, B., Bellanca, A., Neri, R., Roe, M.J., 2001. Trace metal partitioning in Fe–Mn nodules from Sicilian soils, Italy. Chem. Geol. 173, 257–269.

Pansu, M., Gautheyrou, J., 2006. Mineralogical separation by selective dissolution. Handbook of Soil Analysis. Springer, Berlin Heidelberg (167–219 pp.).

Paye, H.D.S., Mello, J.W.V.D., Abrahão, W.A.P., Fernandes Filho, E.I., Dias, L.C.P., Castro, M.L.O., Melo, S.B.D., França, M.M., 2010. Valores de referência de qualidade para metais pesados em solos no Estado do Espírito Santo. Rev. Bras. Ciênc. Solo 34, 2041–2051.

Peng, A., Wang, Z.J., 1995. Recent research progress on environmental chemistry of rare earth elements. Adv. Environ. Sci. 3, 22–32.

Pérez, D.V., Saldanha, M.F.C., Meneguelli, N.A., Moreira, J.C., Vaitsman, D.S., 1997. Geoquímica de alguns solos brasileiros 4. Embrapa Solos, Rio de Janeiro, pp. 1–14.

Pourret, O., Davranche, M., Gruau, G., Dia, A., 2007. Rare earth elements complexation with humic acid. Chem. Geol. 243, 128–141.

Reimann, C., Filzmoser, P., 2000. Normal and lognormal data distribution in geochemistry: death of a myth. Consequences for the statistical treatment of geochemical and environmental data. Environ. Geol. 39, 1001–1014.

Reimann, C., Filzmoser, P., Garrett, R.G., 2005. Background and threshold: critical comparison of methods of determination. Sci. Total Environ. 346, 1–16.

Ruiz, H.A., 2005. Incremento da exatidão da análise granulométrica do solo por meio da coleta da suspensão (Silte + Argila). Rev. Bras. Ciênc. Solo 29, 297–300.

Sabbioni, E., Pietra, R., Gaglione, P., Vocaturo, G., Colombo, F., Zanoni, M., Rodi, F., 1982. Long-term occupational risk of rare-earth pneumoconiosis: a case report as investigated by neutron activation analysis. Sci. Total Environ. 26, 19–32.

Sadeghi, M., Petrosino, P., Ladenberger, A., Albanese, S., Andersson, M., Morris, G., Lima, A.M., De Vivo, B., The Gemas Project Team, 2013. Ce, La and Y concentrations in agricultural and grazing-land soils of Europe. J. Geochem. Explor. 133, 202–213.

Sinclair, A.J., 1983. Univariate analysis. In: Howarth, R.J. (Ed.), Statistics and data analysis in geochemical prospectingHandbook of Exploration Geochemistry vol. 2. Elsevier, Amsterdam, pp. 59–81.

Taylor, S.R., Mclennan, S.M., 1995. The geochemical evolution of the continental crust. Rev. Geophys. 33, 611–627.

Tyler, G., 2004. Rare earth elements in soil and plant systems — a review. Plant Soil 267, 191–206.

U.S. Geological Survey, 2014. Mineral Commodity Summaries 2014 (196 pp.).

Wang, Q., Huang, B., Guan, Z., Yang, L., Li, B., 2001. Speciation of rare earth elements in soil by sequential extraction then HPLC coupled with visible and ICP-MS detection. Fresenius J. Anal. Chem. 370, 1041–1047.

Xing, B., Dudas, M.J., 1993. Trace and rare earth element content of white clay soils of the Three River Plain, Heilongjiang Province, P.R. China. Geoderma 58, 181–199.

Yan, X.-P., Kerrich, R., Hendry, M.J., 1999. Sequential leachates of multiple grain size fractions from a clay-rich till, Saskatchewan, Canada: implications for controls on the rare earth element geochemistry of porewaters in an aquitard. Chem. Geol. 158, 53–79.

Zhang, S., Shan, X.-Q., 2001. Speciation of rare earth elements in soil and accumulation by wheat with rare earth fertilizer application. Environ. Pollut. 112, 395–405.

Zhang, H., Feng, J., Zhu, W., Liu, C., Xu, S., Shao, P., Wu, D., Yang, W., Gu, J., 2000. Chronic toxicity of rare-earth elements on human beings. Biol. Trace Elem. Res. 73, 1–17.

Zhu, Y.G., Shaw, G., 2000. Soil contamination with radionuclides and potential remediation. Chemosphere 41, 121–128.

Zhu, W., Xu, S., Shao, P., Zhang, H., Wu, D., Yang, W., Feng, J., Feng, L., 2005. Investigation on liver function among population in high background of rare earth area in South China. Biol. Trace Elem. Res. 104, 1–7.