



Distribution of rare earth elements in soils of contrasting geological and pedological settings to support human health assessment and environmental policies

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Abstract Establishing quality reference values (QRVs) for rare earth elements (REEs) in soils is essential for the screening of these emergent contaminants. Currently, Brazil has the second-largest reserve of REEs, but data regarding background concentrations and distributions in soils remain scarce. The aim of this study was to establish the QRVs and assess the spatial distribution of REEs in soils, including REE fractionations and anomalies in (Piauí) state (251,529.186 km²), northeastern Brazil. This study reports the most detailed data on REE geochemistry in Brazilian soils. A total of 243 composite soil samples

was collected at 0–20 cm depth. The mean background concentrations in soils followed the abundance of the earth's upper crust: Ce > La > Nd > Pr > Sm > Dy > Gd > Er > Yb > Eu > Tb > Lu. The \sum REEs (mg kg⁻¹) showed the following order based on the individual mesoregions of Piauí state: Southeast (262.75) > North and Central-North (89.68) > Southwest (40.33). The highest QRVs were observed in the Southeast mesoregion. The establishment of QRVs based on the mesoregion scale improves data representativeness and the monitoring of natural REE values by identifying hot spots. Geostatistical modeling indicated significant local variability, especially in the Southeast mesoregion. The levels of these elements in this spatial zone are naturally higher than the other values across Piauí state and the mesoregion itself and indicate a high potential to exceed the QRVs. Our approach provides much needed data to help strengthen policies for both human health and environmental protection.

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Introduction

The rare earth elements (REEs) comprise a group of 15 chemical elements from the lanthanide series. These

elements are found in more than 270 minerals (Huang et al. 2020) and comprise two groups according to their ionic radius: light REE (LREEs; La, Ce, Pr, Nd, Pm, Sm and Eu) and heavy REE (HREEs; Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu), with the corresponding atomic numbers ranging from 57 (La) to 71 (Lu). Light rare earth elements are often more abundant in nature in comparison with HREEs (Zhou, 2017). Rare earth elements distribution is affected by primary and secondary geological processes involving magmatic or metamorphic processes, weathering and sedimentary transport (Dushyantha et al. 2020). Although REEs are found in silicates, carbonates, oxides and phosphates, they do not fit into most mineral structures (Balaram, 2019). The intensity of weathering controls the transformation of minerals that act as sources of REEs in soils and several other environmental compartments (Silva et al. 2018a).

According to the US Geological Service Mineral Commodity Summaries of 2020, Brazil has the second-largest reserve of REEs in the world (~ 22,000,000 t). The extraction of REEs in Brazil is still little explored. Yet, due to global demand, mainly from the industrial and technological sectors, the perspective is that the country might become a global leader in extracting these elements (Zhanheng, 2011). Therefore, the mining and metallurgy of REEs should be monitored to decrease associated environmental degradation and human health hazards (Balaram, 2019).

The QRVs for heavy metals have been established and regulated in several Brazilian states (Almeida Júnior et al. 2016; Biondi et al. 2011; Boechat et al. 2020; Costa et al. 2017; Feitosa et al. 2020; Fernandes et al. 2018; Preston, 2014; Sahoo et al. 2020; Santos & Alleoni, 2013; Silva et al. 2015) and around the world (Chen et al. 1991; Salonen & Korkka-Niemi, 2007; Martinez-Lladó et al. 2008; Alfaro et al. 2015), which has advanced knowledge of the natural patterns of these elements and contributed to environmental monitoring. REE background concentrations are the first step to establish guideline values for monitoring these elements in the environment and supporting future research on anthropogenic impacts related to soil contamination. For REE content in soils, however, there is no regulation and studies with these elements are still scarce (Paye et al. 2016; Pereira et al. 2019; Silva et al. 2020). In this scenario, this study aimed to establish the background concentration, QRVs and

spatial distributions of REEs in soils collected for a large geochemical survey (251,529.186 km²) encompassing different geological, pedological and environmental scales.

Material and methods

Study area and soil sampling

The study area covers the Piauí state, the third-largest state in Brazil's Northeast region, and encompasses a combination of large areas of sedimentary rocks, and smaller portions of igneous and metamorphic bedrocks (Fig. 1). The climate varies from sub-humid (800–1600 mm) in the Northern and Southwestern areas to semiarid (400–600 mm) in the Southeastern (Andrade Junior et al. 2005). The annual average air temperatures range from 26 to 30 °C. Furthermore, the study area lies in the transition zones of three of the main Brazilian biomes: Cerrado, Amazon and Caatinga. Soils are mainly Oxisols, Entisols and Ultisols.

Soil samples were collected at sites under natural vegetation, with minimal anthropic influence, covering the geological and pedological diversity of the state (Fig. 1). A total of 243 composite soil samples were collected at 0–20 cm depth. Each composite soil sample was composed of five subsamples. The composite soil samples were air-dried, homogenized, dry-sieved through a 2-mm mesh and passed through a 0.3-mm mesh stainless steel sieve (ABNT n^o. 50).

Determination of REEs and quality control

Samples were digested in Teflon vessels (12 mL acid solution—HNO₃/HCl, 3:1) in a microwave oven (USEPA 1998). Standard operational and analytical data quality assurance procedures were followed, including the use of calibration curves, high-purity acids, curve recalibration, analysis of reagent blanks and standard reference materials (2709a San Joaquin Soil and 2710a Montana I Soil; NIST 2002). Concentrations of REEs were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). In order to improve the sensitivity to REE content, we coupled a cyclonic spray chamber/nebulizer to the ICP-OES. Recovery rates ranged from 83 to 105%. Some low recoveries were expected because this study determined the environmentally available

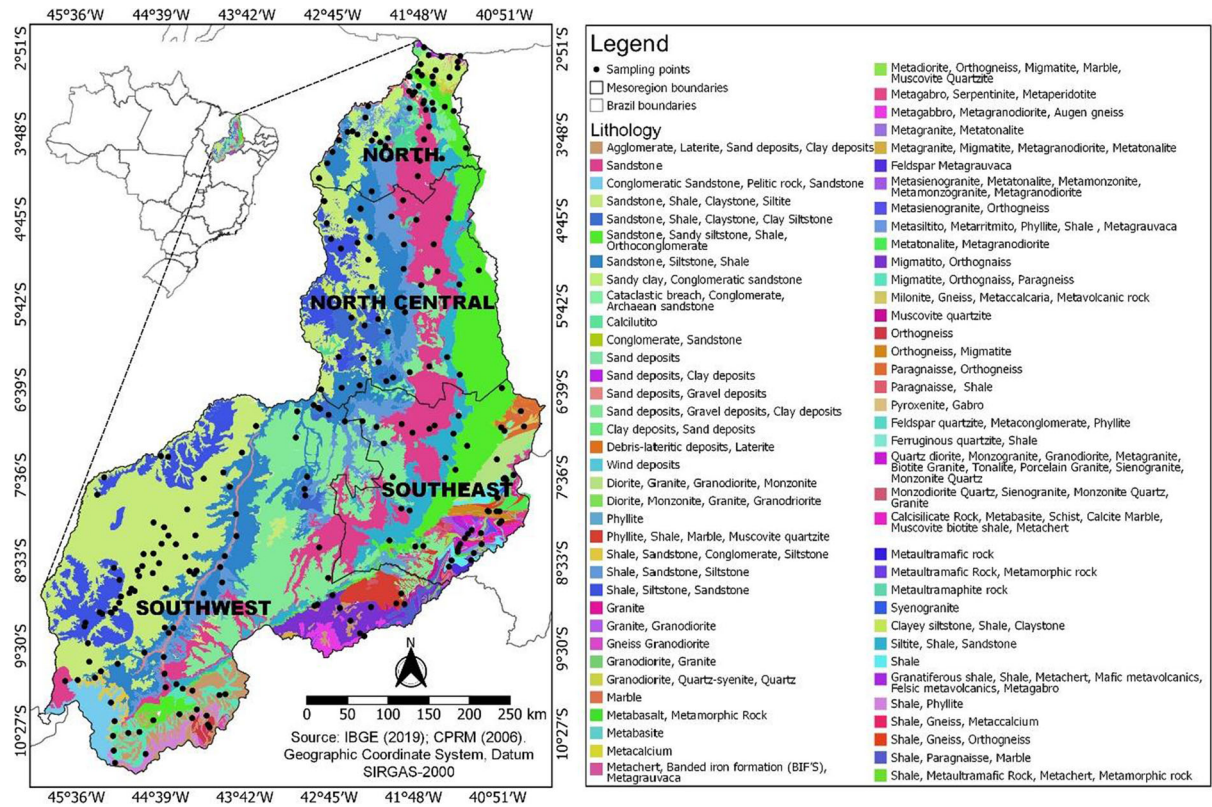


Fig. 1 Geological map of Piauí state, Northeastern Brazil

(leachable) concentrations, whereas the NIST certificate values are total concentrations. This digestion method releases the REE concentrations that will become available in the medium and long term. The extraction encompasses the environmentally relevant fractions, such as the REE concentrations in sulfates, oxides, carbonates and less labile phases (USEPA, 1998; Rao et al. 2010; Löll et al. 2011; Alfaro et al. 2015; Feitosa et al. 2020). All analyses were performed in duplicate.

Fractionation and anomalies

Soil samples were normalized to the Upper Continental Crust (Taylor & McLennan, 1985, mg kg⁻¹): La (30); Ce (64); Pr (7.1); Nd (26); Sm (4.5); Eu (0.88); Gd (3.8); Tb (0.64); Dy (3.5); Ho (0.8); Er (2.3); Tm (0.33); Yb (2.2); Lu (0.32). Fractionation between LREEs and HREEs was calculated according to $\sum LREE / \sum HREE$ and La_N / Yb_N ratios. The anomalies of Ce [(Ce_N / (La_N * Pr_N)^{0.5})] and Eu [(Eu_N / (Sm_N * Gd_N)^{0.5})] were calculated according to Compton et al.

(2003), where N implies normalized values. A value below “1” (negative anomaly) represents depletion, while a value above “1” (positive anomaly) means enrichment compared to the reference material used.

Chemical and physical analyses

The pH values were analyzed in H₂O (1:2.5 soil/solution ratio). Exchangeable K⁺ and Na⁺ were obtained by flame emission photometry after extraction with Mehlich-1. Exchangeable Ca²⁺, Mg²⁺ and Al³⁺ were obtained by titration after extraction with 1 mol L⁻¹ KCl (Donagema et al. 2011). The results obtained from the sorptive complex were used to calculate the values for the sum of bases (SB) and cation exchange capacity (CEC). Organic carbon (OC) was determined by the Walkley–Black method. The particle size distribution was obtained according to Gee and Or (2002).

Statistical analysis

Descriptive statistics, Pearson's correlation and discriminant analysis were used in this study. Quality reference values were established based on the 75th percentile and the exclusion of anomalous values following the national regulation (CONAMA 420/2009). The 75th percentile is adopted in most studies of QRVs and prioritized by governmental and environmental institutions in Brazil, since it meets its standardization more rigidly and avoids the insertion of anomalous values (Nogueira et al. 2018; Santos & Alleoni, 2013). Geostatistical modeling was used to evaluate the spatial distribution of the REE contents. The adjustment models of the experimental semivariograms were selected taking into account the Akaike's Information Criterion (AIC). The degree of spatial dependence (DSD) was calculated following Cambardella et al. (1994) [$C0/(C0 + C1) \times 100$]. A nugget effect less than, or equal to, 25% of the plateau was considered strong. The value was considered moderate when it ranged from 25 to 75% and weak when greater than 75%. Variables showing DSD lower than a unit were not considered. All geostatistical procedures were carried out using R software (R CORE TEAM 2019; Ribeiro Jr, 2020).

Results and discussion

Background concentrations and QRVs of REEs in soils

The average background concentrations of REEs in Piauí state (PI) followed the standard contents for the upper continental crust (Table 1), reflecting the greater abundance of REEs with even atomic numbers (Oddo-Harkins rule) (Laveuf & Cornu, 2009; Tyler & Olsson, 2002): $Ce > La > Nd > Pr > Sm > Dy > Gd > Er > Yb > Eu > Tb > Lu$. This order was slightly different for dysprosium (Dy) and gadolinium (Gd), due to the seemingly low natural enrichment of these elements in the study area. The coefficients of variation (CV) ranged from 135.47% (Pr) to 197.54% (Dy) showing the geochemical heterogeneity of the study soils. The LREEs accounted for 93% of the total REEs. Cerium, La and Nd accounted for 44%, 21% and 17% of the total REE concentration. This pattern has been observed for other Brazilian soils

(Table 1). Besides, Ce showed natural background concentrations higher than other metals in soils of PI, including Ba, Cr, Ni, Pb, V and Zn (Boechat et al. 2020).

In general, the average value for $\sum REEs$ (107.8 mg kg^{-1}) was lower than that found in the Upper Continental Crust (UCC) (Tyler & Olsson, 2002), Europe (Sadeghi et al. 2013) and China (Wei et al. 1991) but higher than that reported for Cuba (Alfaro et al. 2018) and Sweden (Sadeghi et al. 2013) (Table 1). The $\sum REE$ values in PI were also lower than those values observed in other Brazilian regions (Paye et al. 2016) and higher in comparison with the other NE Brazil states such as Pernambuco and Rio Grande do Norte (Silva et al. 2016, 2018a, 2018b).

Based on the REE geochemistry, we grouped the soil samples into three regions. Given their similarities, North and North-Central were merged (Fig. 2). The first two factors explained approximately 92% ($F1 = 82\%$ and $F2 = 10\%$) of the REE variation in the sampled soils. F1 was mainly influenced by LREEs (i.e., Sm, Gd, Nd, Pr, Ce and La), while F2 was more correlated with HREEs (Lu, Yb, Er, Dy, Tb and Eu). The mesoregions were classified as follows: Southwest 100%; North-Central 33,3%; North 25% and Southeast 52,7%, further justifying the establishment of QRVs based on a mesoregion scale. As demonstrated, the North-Central and North mesoregions are more correlated and thus were merged.

Southwestern and Southeastern showed the lowest and highest REE concentrations, respectively (Table 2). Such values were above the REE concentrations reported for the states and countries displayed in Table 1. Indeed, the REE concentrations in the Southeastern mesoregion ($\sum REEs = 262.75 \text{ mg kg}^{-1}$) were similar to those found in volcanic soils (Feitosa et al. 2020). The highest QRVs were also observed in the Southeastern region. The establishment of QRVs based on mesoregions improved data resolution, based on the high variability of the values. It also enhanced the assessment of natural REE values by identifying hot spots (Table 2).

Fractionation and anomalies of Ce and Eu

The La/Yb_N ratio showed that fractionation between LREEs and HREEs decreased in the following order: North and North-Central (5.3) > Southeast

Table 1 Average REE concentrations (mg kg⁻¹) in soils from Piauí state (PI) and other values reported for Brazil and elsewhere worldwide

REEs	PI	RN ¹	PE ²	Cuba ³	China ⁴	Sweden ⁵	Europe ⁵	UCC ⁶
La ⁽⁵⁷⁾	23.1	18.9	20.8	15.2	37.4	17.4	25.9	35.0
Ce ⁽⁵⁸⁾	47.8	40.4	43.5	24.2	64.7	37.7	52.2	66.0
Pr ⁽⁵⁹⁾	6.1	7.3	9.6	5.03	6.7	4.1	6.0	9.1
Nd ⁽⁶⁰⁾	19.0	15.8	17.7	17.1	25.1	15.1	22.4	40.0
Sm ⁽⁶²⁾	3.6	3.0	3.4	4.7	4.9	3.0	4.3	7.0
Eu ⁽⁶³⁾	0.6	0.5	0.6	0.03	1.0	0.7	0.9	2.1
Gd ⁽⁶⁴⁾	1.8	2.6	2.3	0.2	4.4	3.1	4.2	6.1
Tb ⁽⁶⁵⁾	0.4	0.5	0.5	1.2	0.6	0.5	0.6	1.2
Dy ⁽⁶⁶⁾	2.9	1.0	0.9	1.3	3.9	3.0	3.6	4.5
Er ⁽⁶⁸⁾	1.0	0.7	0.6	2.4	2.4	1.9	2.1	3.5
Yb ⁽⁷⁰⁾	0.8	0.6	0.7	1.9	2.3	2.0	2.1	3.1
Lu ⁽⁷¹⁾	0.2	0.2	0.1	0.8	0.4	0.3	0.3	0.8
∑LREEs	100.4	86.0	95.6	65.9	139.8	78.0	111.7	159.2
∑HREEs	7.4	5.9	5.2	8.2	14.8	11.3	13.6	20.5
∑REEs	107.8	91.9	100.8	74.2	154.6	89.3	125.3	179.7
∑LREEs/∑HREEs	13.5	14.5	18.3	8.0	9.4	6.9	8.2	7.8

¹Silva et al. (2018b); ²Silva et al. (2016); ³Alfaro et al. (2018); ⁴Wei et al. (1991); ⁵Sadeghi et al. (2013); ⁶Tyler and Olsson (2002).
 RN, Rio Grande do Norte; PE, Pernambuco; UCC, Upper Continental Crust

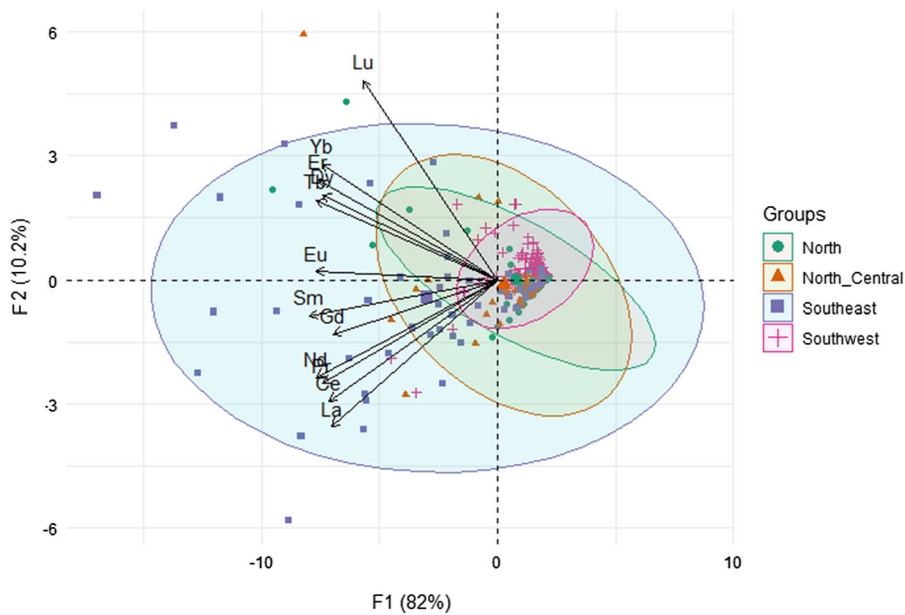


Fig. 2 Discriminant analysis of the concentrations of REEs in soils of Piauí state (PI), Northeastern Brazil

(3.3) > Southwest (1.4) (Table 3), with an influence of the contrasting geological settings (Fig. 1). In the Southwest region, the low La/Yb_N ratios are due to the predominance of soils derived from detrital sedimentary rocks, such as sandstones, siltstones, shales and limestones (Pfaltzgraff et al. 2010) (Fig. 1). Low REE contents have been reported for soils originating from quartz sandstones (Taylor & McLennan, 1985)

(Table 2). Soils originating from sedimentary rocks generally have lower fractionation between LREEs and HREEs than soils derived from igneous rocks (Paye et al. 2016; Pereira et al. 2019; Silva et al. 2016, 2018a, 2018b).

The significant variation in the fractionation between LREEs and HREEs in the soils of the North and North-Central mesoregions results from the

Table 2 Average, minimum and maximum concentrations, and QRVs (P 75) of REEs by mesoregions of Piauí state (PI), North-eastern Brazil

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Er	Yb	Lu
Piauí State (n = 243 – all samples)												
Mean	23.19	48.10	6.17	19.09	3.64	0.68	1.81	0.49	2.97	1.07	0.87	0.25
Min	0.65	1.13	nd	0.05	0.10	nd	nd	nd	nd	nd	nd	nd
Max	227.40	377.10	46.10	155.00	33.00	5.80	29.15	5.10	51.30	14.35	11.00	2.35
n (1)	217	213	222	213	216	211	210	215	206	217	216	225
n (2)	26	30	21	30	27	32	33	28	37	26	27	18
QRVs	18.15	39.04	5.21	14.28	2.76	0.45	1.06	0.35	1.46	0.63	0.54	0.25
North and North-Central (n = 87)												
Mean	19.15	42.05	4.83	14.97	2.76	0.49	0.95	0.34	2.53	0.82	0.61	0.18
Min	0.83	1.40	0.10	0.43	0.23	nd	nd	nd	0.05	nd	nd	nd
Max	96.10	220.55	25.70	84.15	17.45	4.45	12.00	3.40	23.60	9.05	8.00	2.35
n (1) ⁽¹⁾	81	81	78	77	78	79	80	75	76	78	78	75
n (2) ⁽²⁾	6	6	9	10	9	8	7	12	11	9	9	12
QRVs	21.25	46.73	4.55	14.69	2.45	0.35	0.83	0.15	1.68	0.55	0.35	0.03
Southeast (n = 55)												
Mean	58.70	113.85	13.63	47.16	8.74	1.71	4.69	1.03	8.03	2.69	2.14	0.38
Min	2.95	7.65	0.60	0.05	0.30	nd	nd	nd	0.30	0.20	0.10	nd
Max	227.40	377.10	46.10	155.00	33.00	5.80	29.15	5.10	51.30	14.35	11.00	1.90
n (1)	54	52	54	55	54	55	52	54	53	52	49	47
n (2)	1	3	1	0	1	0	3	1	2	3	6	8
QRVs	80.53	144.95	18.00	72.25	12.54	2.55	5.53	1.44	9.33	2.84	2.00	0.35
Southwest (n = 101)												
Mean	7.34	17.51	3.27	7.36	1.63	0.27	0.98	0.31	0.60	0.41	0.39	0.25
Min	0.65	1.13	nd	0.48	0.10	nd	nd	nd	nd	nd	0.05	nd
Max	87.45	165.78	34.10	72.45	13.25	1.30	7.20	1.58	4.25	2.33	2.25	1.15
n (1)	88	91	91	90	91	94	94	92	92	90	91	97
n (2)	13	10	10	11	10	7	7	9	9	11	10	4
QRVs	4.97	12.73	2.20	5.42	1.38	0.28	0.83	0.35	0.49	0.36	0.40	0.35

Max = Maximum; Min = Minimum; nd = non detected; P(75) = 75th percentile; ⁽¹⁾Samples used to obtain the QRVs; ⁽²⁾Anomalous samples using observations of boxplot graphs

predominance of soils derived from basalt, diabase, sandstone and conglomerates associated with siltite and argillite, siltstones, shales and limestones (CPMR 2009; Pfaltzgraff et al. 2010). In general, the smallest and largest fractionations were found in soils originating from sedimentary and igneous rocks. The fractional crystallization of magma is the probable reason for the enrichment of LREEs in soils derived from igneous rocks (Laveuf & Cornu, 2009) (Table 3). Soils derived from sandstones in Iran also exhibited low REE fractionation (Tazikeh et al. 2018).

The fractionation between LREEs and HREEs in the Southeast mesoregion of PI ranged from 0.5 to 12.6, with an average of 3.3 (Table 3). Soils derived from the igneous-metamorphic basement, characterized by two main groups: i) migmatites, orthogneisses and metagranites of the Archean and Paleoproterozoic ages, and; ii) shales and quartzites of the Ipeueirinha group, showed the highest values. On the other hand, the lowest fractionation between LREEs and HREEs occurred in soils derived from metasedimentary rocks (Pfaltzgraff et al. 2010).

Table 3 Normalized REE concentrations, and Ce and Eu anomalies in surface soils of the North and North-Central (n = 87), Southeast (n = 55), and Southwest (n = 101), mesoregions of Piauí state (PI), Northeastern Brazil

Variable	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	La/YbN	Ce*	Eu*
North and North-Central																	
Mean	0.6	0.7	0.7	0.6	0.6	0.6	0.3	0.5	0.7	nd	0.4	nd	0.3	0.6	5.3	1.0	0.9
Minimum	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.7	nd
Maximum	3.2	3.4	3.6	3.2	3.9	5.1	3.2	5.3	6.7	nd	3.9	nd	3.6	7.3	22.8	1.7	5.8
SD	0.4	0.5	0.5	0.4	0.5	0.5	0.3	0.6	0.7	nd	0.4	nd	0.3	0.8	3.5	0.1	0.7
Southeast																	
Mean	2.0	1.8	1.9	1.8	1.9	1.9	1.2	1.6	2.3	nd	1.2	nd	1.0	1.2	3.3	1.0	1.1
Minimum	0.1	0.1	0.1	nd	0.1	nd	nd	nd	0.1	nd	0.1	nd	nd	nd	0.5	0.5	nd
Maximum	7.6	5.9	6.5	6.0	7.3	6.6	7.7	8.0	14.7	nd	6.2	nd	5.0	5.9	12.6	1.6	2.7
SD	1.4	1.2	1.3	1.3	1.4	1.4	1.1	1.3	1.8	nd	0.9	nd	0.8	1.1	1.8	0.2	0.5
Southwest																	
Mean	0.2	0.3	0.5	0.3	0.4	0.3	0.3	0.5	0.2	nd	0.2	nd	0.2	0.8	1.4	1.0	1.6
Minimum	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.2	nd	nd
Maximum	2.9	2.6	4.8	2.8	2.9	1.5	1.9	2.5	1.2	nd	1.0	nd	1.0	3.6	9.5	3.4	8.0
SD	0.2	0.2	0.5	0.3	0.3	0.2	0.3	0.4	0.2	nd	0.2	nd	0.1	0.5	0.7	0.2	0.8

SD = standard deviation; nd = non detected

In general, there is no Ce anomaly in the soils, as demonstrated by values equal to 1 for all mesoregions (Table 3). These results show the low enrichment or depletion of Ce in these soils. Silva et al. (2018a, 2018b) also observed an average Ce anomaly close to unity studying soils under different geological and climate patterns of NE Brazil. Soils derived from schists and phyllites in the Southwest mesoregion showed the highest positive Ce anomaly (Ce* = 3.4). The mean Eu* values followed the order: Southwest (1.6) > Southeast (1.1) > North and North-Central (0.9) (Table 3). The higher positive Eu anomalies occurring in soils are formed from igneous and metamorphic rocks in the Southwestern mesoregion.

The lithological structure of the Southeast mesoregion is the most variable (Fig. 1). Such lithology is mainly composed of the Ipeirinha formations (migmatites, metagranite orthogneisses, shales and quartzites), Barra Bonita (metasedimentary rocks, such as phyllites, marbles, shales and quartzites) and by the Itaporanga Suite (diorites, granodiorites and monzonites) (Pfaltzgraff et al. 2010). The mesoregion also exhibits mafic-ultramafic and vulcanosedimentary units with a legacy of mining activities (Pfaltzgraff et al. 2010; Caxito et al. 2013).

Influence of soil properties on REE geochemistry

In general, soils are acidic (mean pH = 4.7), sandy (mean sand = 72.9%), with low organic matter content (SOC = 0.9 dag kg⁻¹), and with an average CEC of 5.9 cmol_c dm⁻³ (Boechat et al. 2020). The North and North-Central region exhibits marked pedological diversity. In contrast, the Southeastern part comprises Oxisols, Ultisols and Inceptisols, and the Southwest region is mainly composed of Oxisols (Jacomine, 1983). Strong positive correlations were observed among REEs and SB, CEC, and silt, whereas a negative correlation was observed between REEs and sand for all mesoregions (Table 4). The REEs of the North and North-Central and Southeast mesoregions showed significant relationships with clay contents. The correlation between the variation in SOC and REEs was minimal, except for the Southeast region, which registered significantly positive correlations. However, it is worth noting that the average levels were low (mean = 0.69%), limiting its influence on REE distribution.

Although the high levels of REEs in the Southeastern are associated with lithological enrichment, the surface soils characteristics seem to contribute to retaining these elements as pointed out by the average

Table 4 Correlation between REEs and soil properties according to mesoregions of Piauí state (PI), Northeastern Brazil. Bold ($p < 0.05$), and bold and italic ($p < 0.01$)

	Al	SB	CEC	pH	SOC	Sand	Silt	Clay
G1—North and North-Central								
\sum REEs	0.27	0.48	0.49	0.23	0.20	– 0.57	0.54	0.30
\sum LREEs	0.29	0.48	0.50	0.21	0.19	– 0.55	0.53	0.28
\sum HREEs	0.05	0.33	0.33	0.34	0.18	– 0.60	0.48	0.42
G2—Southeast								
\sum REEs	– 0.38	0.44	0.44	0.56	0.30	– 0.63	0.58	0.26
\sum LREEs	– 0.39	0.42	0.42	0.55	0.29	– 0.63	0.58	0.24
\sum HREEs	– 0.15	0.49	0.49	0.45	0.34	– 0.54	0.40	0.39
G3—Southwest								
\sum REEs	– 0.24	0.72	0.72	0.68	– 0.22	– 0.28	0.21	0.16
\sum LREEs	– 0.23	0.71	0.71	0.68	– 0.22	– 0.27	0.20	0.16
\sum HREEs	– 0.24	0.84	0.84	0.63	– 0.14	– 0.46	0.43	0.18

Al, aluminum; SB, sum of bases; SOC, soil organic carbon; CEC, cation exchange capacity

CEC of $8.88 \text{ cmol}_c \text{ dm}^{-3}$ in the Southeastern as compared to the $6.48 \text{ cmol}_c \text{ dm}^{-3}$ and $3.95 \text{ cmol}_c \text{ dm}^{-3}$ CECs of the North and North-Central and Southwest regions, respectively. Besides, soil pH close to neutrality and semiarid climate in the Southeastern favors adsorption and decrease REEs leaching (Júnior et al. 2004).

Spatial distribution of REEs in soils

The selection of the theoretical model of the semivariograms was made based on the lowest value of the AIC. The experimental semivariograms showed no difference in variability based on changing directions. The selected models (Table 5) ranged from circular (\sum LREEs and \sum HREEs), Gaussian (\sum REEs) and exponential (\sum LREEs/ \sum HREEs). Exponential and spherical models are often used in soil science studies (Grego & Vieira, 2005; Pereira et al. 2019), but other models can be chosen based on AIC and DSD. According to the parameters of the semivariograms and the classification of Cambardella et al. (1994), all

variables showed moderate spatial dependence. The results for LREEs and HREEs indicated different spatial characteristics and effects of spatial randomness. The \sum LREEs showed greater spatial dependence over wide areas (239.18 km) to the detriment of the \sum HREEs. This points to the need for extending the sample grid for the spatial characterization of HREEs (Chen et al. 2019). Moreover, the lower DSD and the range of the \sum LREEs/ \sum HREEs indicated greater spatial variability of this relationship and greater formation of spatial nuclei among the REEs in the territory of PI.

The maps of the sum of the REEs in the sampled soils showed substantial spatial variability in the Southeastern mesoregion (Fig. 3), with marked variations in the content of the REEs in the west–east direction. The Southeast mesoregion also expressed the highest levels of REEs in the state, especially in the soils of the eastern portions, where the estimated \sum REEs ranged from 400 to 600 mg kg^{-1} . These values indicate natural hot spots with high potential to surpass the state and regional QRVs. Homogeneous

Table 5 Theoretical models and parameters of semivariograms of \sum REEs, \sum LREEs, \sum HREEs and \sum LREEs/ \sum HREEs

REEs	Model	β_0	β_1	β_2	Range (km)	Partial sill	Nugget	AIC	DSD (%)
\sum LREEs	Circular	2.716	0.006	– 0.003	239.18	0.409	0.656	2,493.119	61.60
\sum HREEs	Circular	0.417	0.005	– 0.003	190.12	0.435	0.959	1,233.223	68.79
\sum REEs	Gaussian	2.949	0.006	– 0.003	153.67	0.499	0.709	2,529.327	58.69
\sum LREEs/ \sum HREEs	Exponential	2.137	0.001	0.0006	17.805	0.106	0.106	1,655.060	50.00

AIC, Akaike's Information Criterion; DSD, = degree of spatial dependence

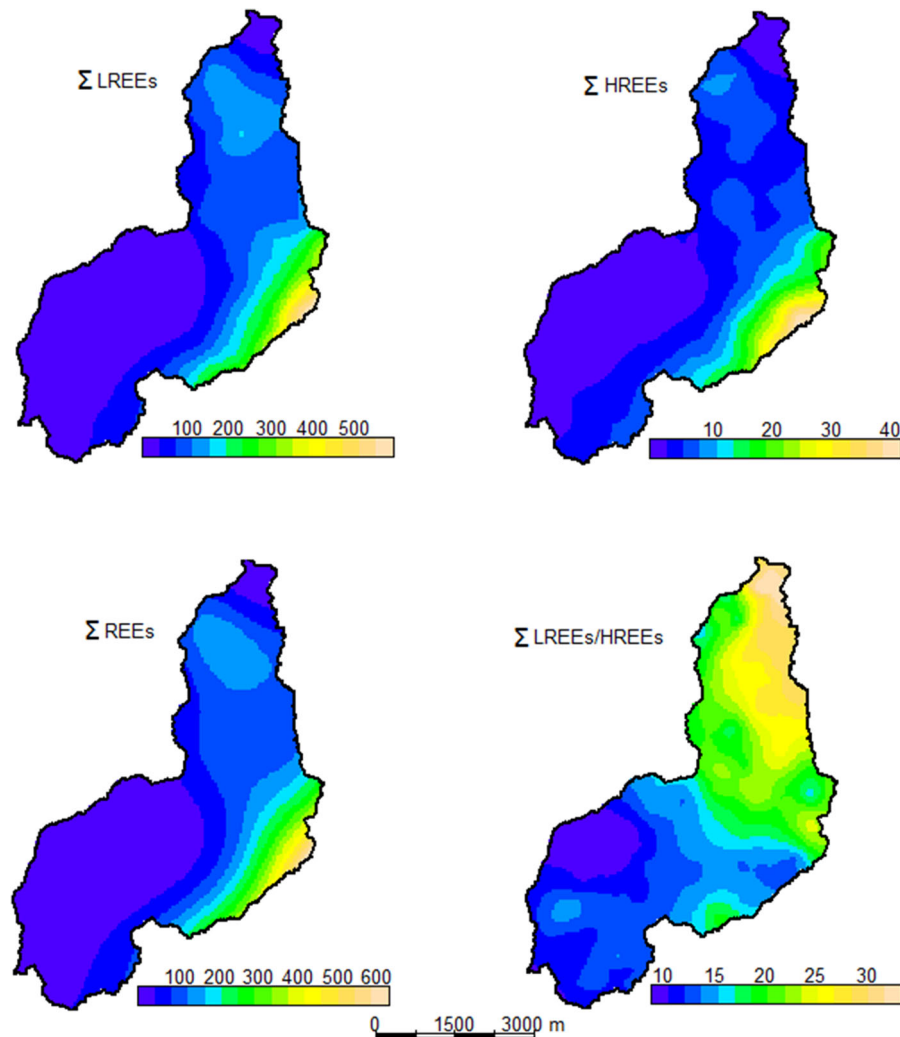


Fig. 3 Distribution maps of Σ REEs, Σ LREEs, Σ HREEs (mg kg^{-1}) and Σ LREEs/ Σ HREE in soils from Piauí state (PI), Northeastern Brazil

patterns of these elements were verified in the North and North-Central and Southwestern mesoregions. The Southwestern mesoregion showed low levels of REEs, normally not exceeding 50 mg kg^{-1} of Σ REEs. The North and North-Central mesoregions also had coldspots, mainly for HREE. The Σ LREEs/ Σ HREEs ratio was markedly variable, ranging from 10 to 30, with significant fluctuations within the mesoregions (Fig. 3). The North and North-Central mesoregions showed the highest Σ LREEs/ Σ HREEs (20–30). This is probably related to the lowest values for HREEs in these particular soils since LREE values did not show significant fluctuations.

Rocks from the eastern part of the Southeastern mesoregion had REE concentrations ranging from 136.47 to 354 mg kg^{-1} , showing enrichment of LREEs mainly in the Paulistana complex (Santos et al. 2017). This geological complex includes a set of shales and aluminous phyllites, and less occurrence of meta-ultramafic bedrocks, quartzites, metaconglomerates, metacherts and tourmalinites (Santos et al. 2017). This suggests the influence of metasedimentary rocks on the soils’ geochemical signature, as well as on the higher concentration of REEs in the eastern part of the Southeastern mesoregion.

Conclusion

The REEs concentrations in the soils varied considerably between the mesoregions of PI. The Southeast mesoregion had high natural levels of REEs, with average values more elevated than in other Brazilian states and some countries. Quality reference values were specifically established in three mesoregions due to the substantial geochemical variation of REEs in PI. The establishment of QRVs based on a mesoregion scale is the most appropriate for PI due to the state's environmental heterogeneity and the substantial variability of REEs. The approach reported in this study can also be applied in other Brazilian states or other areas exhibiting similar variability of REEs, which strengthens the resolution of the data and assists regulatory institutions, facilitating the discrimination of the enrichment (anthropic or natural) of REEs in soils. Geostatistical modeling indicated significant local variability, especially in the Southeast mesoregion. The levels of these elements in this particular area are naturally higher than other values for the state and the mesoregion itself and indicate a high potential to exceed the QRVs. Future studies should seek to improve the resolution of the soil sampling, with a view to developing new more local QRVs, taking into account the specific geochemical characteristics.

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Declarations

Conflict of interests The authors declare that they have no competing interests.

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