Rare earth elements (REEs): geochemical patterns and contamination aspects in Brazilian benchmark soils[☆]

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ABSTRACT

Rare earth elements have been increasingly used in modern societies and soils are likely to be the final destination of several REE-containing (by)products. This study reports REE contents for topsoils (0–20 cm) of 175 locations in reference (n = 68) and cultivated (n = 107) areas in Brazil. Benchmark soil samples were selected accomplishing a variety of environmental conditions, aiming to: i) establishing natural background and anthropogenic concentrations for REE in soils; ii) assessing potential contamination of soils - via application of phosphate fertilizers - with REE; and, iii) predicting soil-REE contents using biomes, soil type, parent material, land use, sand content, and biomes-land use interaction as forecaster variables through generalized least squares multiple regression. Our hypotheses were that the variability of soil-REE contents is influenced by parent material, pedogenic processes, land use, and biomes, as well as that cultivated soils may have been potentially contaminated with REE via input of phosphate fertilizers. The semi-total concentrations of REE were assessed by inductively coupled plasma mass spectrometry (ICP-MS) succeeding a microwave-assisted aqua regia digestion. Analytical procedures followed a rigorous QA/QC protocol. Soil physicochemical composition and total oxides were also determined. Natural background and anthropogenic concentrations for REE were established statistically from the dataset by the median plus two median absolute deviations method. Contamination aspects were assessed by REE-normalized patterns, REE fractionation indices, and Ce and Eu anomalies ratios, as well as enrichment factors. The results indicate that differences in the amounts of REE in cultivated soils can be attributed to land use and agricultural sources (e.g., phosphate-fertilizer inputs), while those in reference soils can be attributed to parent materials, biomes, and pedogenic processes. The biomes, land use, and sand content helped to predict concentrations of light REE in Brazilian soils, with parent material being also of special relevance to predict heavy REE contents in particular.

1. Introduction

Rare earth elements (REEs) have been increasingly employed in activities of our society due to their multiple applications, including their use in many modern industries, as well as in agriculture and medicine (Reimann and de Caritat, 2017; Neves et al., 2018; Alfaro et al., 2018; Moreira et al., 2019). Although very useful, REE can be considered emerging contaminants in soil environments not only because of inadequate discharge of REE-rich wastes in soils worldwide, but also due to

their occurrence in phosphate fertilizers that are used in several agroecosystems (Ramos et al., 2016a; Dinali et al., 2019; Silva et al., 2019). Since an increase in REE contents in soils - including agricultural frontiers - may lead to bioaccumulation in plants, thus posing risk to the environment and human health, addressing REE inputs, geochemical background, occurrence, and fate in different biomes is strategic as there is still very limited knowledge about the biological role of REE (Ramos et al., 2016b; Zaharescu et al., 2017).

The lanthanides comprise most of the REE series (La to Lu)

(Dołęgowska and Migaszewski, 2013). Most Earth scientists exclude Sc from lanthanides because of its small ionic radius, and classify only lanthanides as REEs, and occasionally Y is included. In contrast, the International Union of Pure and Applied Chemistry (IUPAC) includes both Y and Sc in the REE group. Although they present similar physical and chemical characteristics, REE are commonly divided into light (LREE: La to Eu) and heavy (HREE: Gd to Lu) ones (Tyler, 2004; Han et al., 2017), as they may have contrasting behavior in some geochemical contexts. On the other hand, some researchers have recently proposed the following REE division: LREE (La–Pm), MREE (Sm–Dy), and HREE (Ho–Lu) (Grawunder et al., 2014; Migaszewski et al., 2016). For the purpose of this study, the REEs were divided into LREE (La to Eu) and HREE (Gd to Lu), and the medium REE (MREE: Sm to Dy) subgroup partly overlaps LREE and HREE. During weathering, REE are distributed in soils according to their stability, nature, and differential dissolution of REE-bearing minerals (Ling et al., 2015; Silva et al., 2017), as well as parent materials - silicates, carbonates, fluorides, phosphates, and others (Laveuf and Cornu, 2009; Sadeghi et al., 2013b).

Since vast areas under native vegetation have been converted into farmlands (Lapola et al., 2014; Guilherme et al., 2018), phosphate fertilizers have been extensively applied in cropping systems, especially in tropical soils/agroecosystems that are well-known for their low native phosphorus (P) content, high P demand, and high P-fixing capacity (Lopes and Guilherme, 2016; Withers et al., 2018). In fact, in many Brazilian agroecosystems, there may be an involuntary input of REE in soils by addition of P fertilizers that may contain high REE levels (Hu et al., 2006; Ramos et al., 2016a, 2016b; Silva et al., 2019). Intense agricultural activity and the need of phosphated inputs containing high REE amounts require the knowledge of soil-REE concentrations covering a wide range of Brazilian soils developed under different environmental conditions.

The geochemical or natural (geogenic) background of soil-REE concentrations are dependent on geological/geochemical context and pedogenic processes, while anthropogenic ones could be influenced by agricultural inputs especially in the soil surface (Matschullat et al., 2000; Hu et al., 2006; Gałuszka, 2007; Turra et al., 2011; Desaules, 2012). Trace elements concentration - REE included - can be highly dependent on soil type, land use (including anthropogenic action), soil-forming factors (climate, organisms, topography, parent material, and time) (Mikkonen et al., 2017; Mihajlovic and Rinklebe, 2018) and pedogenic processes, being well expressed in differential biomes linked to prevailing environmental conditions (Menezes et al., 2020). Geochemistry studies about soil-REE contamination by agricultural inputs are still scarce, especially when compared with available data for trace elements with environmental interest (Matschullat et al., 2012; Schucknecht et al., 2012; Sá Paye et al., 2016; Silva et al., 2016; Ferreira et al., 2021).

The distinction between natural background and anthropogenic REE concentrations in soils is required for environmental risk assessments and for evaluating potential soil contamination via agricultural use, notably by addition of phosphate inputs (Desaules, 2012; Esmaeili et al., 2014; Mikkonen et al., 2017). In this study, the knowledge of geochemical background concentration for REE is the first step in our approach to discriminate natural (geogenic) from anthropogenic sources (Matschullat et al., 2000; Reimann and de Caritat, 2017; Yotova et al., 2018). Moreover, the REE dataset used in our investigation accounts for a wide variation of environments, providing information linking different soil-forming factors to pedogenic processes, allowing for a better understanding on the impacts of human activities and natural variations on soil geochemistry (Rothwell and Cooke, 2015). Our first hypothesis is that the variability of soil-REE concentrations is strongly influenced by parent material, pedogenic processes, land use, and biomes. Secondly, agricultural soils may have been potentially contaminated with REE mainly due to the use phosphate inputs.

We evaluated REE concentrations in benchmark soils derived from different soil parent materials and biomes, encompassing native and agricultural ecosystems, aiming to: i) establishing natural background and anthropogenic concentrations for REE in soils; ii) assessing contamination aspects of REE in cultivated soils due to application of phosphate fertilizers and phosphogypsum (hereafter sometimes called phosphate products); and, iii) predicting models in order to better understand the most relevant environmental factors that could explain the variation on soil-REE concentrations.

2. Materials and methods

2.1. Dataset characteristics

A total of georreferenced 175 topsoil (0–20 cm) samples were selected from a soil-profiles legacy databank of the Brazilian Agricultural Research Corporation (Soil Science Division) (geographic coordinates of samples can be found in Supplementary material – Table S1). They represent benchmark soils developed under different environmental conditions, accomplishing a wide variation of soil types, parent materials, biomes, and climate characteristics throughout Brazilian territory (Fig. 1 and Table 1). Based on the low density of sampling, this dataset presents a great variation of soil-forming factors and pedogenic processes.

The soils were classified according to WRB/FAO (IUSS Working Group WRB, 2014). Selected samples were taken in reference soils (under pristine control areas, $n = 68$) to establish geochemical or natural (geogenic) background concentration for REEs. Additional samples ($n = 107$) were taken in cultivated soils to establish non-natural or anthropogenic concentration and to verify the contamination aspects by soil-REE via agricultural exploration with a record of long-term application of phosphate inputs. All soils were characterized by means of traditional lab analyses (fertility, organic carbon, and particle size distribution), proximal sensor (portable X-ray fluorescence - pXRF), and ICP-MS (REE concentration). The quality and accuracy of chemical analyses were assessed and are presented in the Supplementary Material.

2.2. Samples digestion for REE quantification

All soil samples were air-dried, homogenized, ground, and 0.05-mm sieved prior to the acid digestion procedure. Soil samples and certified reference material (CRM) were digested according to the USEPA 3051 A method (USEPA, 2007) into a programmable microwave digester CEM-Mars 6 (Mars Xpress, CEM Corporation, Matthews, NC, USA) using Teflon Xpress tubes. The conditions within each vessel were monitored and controlled by means of an infrared sensor.

For the semi-total REE quantification, the acid digestion procedure was conducted with a mixture of 0.500 g of each sample or CRM and 10 mL of HNO_3–HCl (hereafter denoted modified aqua regia 3:1, v/v) being transferred to Teflon tubes, which were filled with ultrapure water (Milli-Q system) to 20 mL. The tubes were maintained in a closed system (Marx Xpress microwave oven) for 20–25 min on the temperature ramp for the necessary time to reach 180 °C. This temperature was maintained during 4 min and 30 s. After digestion, the extracts from soil samples and CRM were taken into centrifuge tubes, filtered and diluted with ultrapure water to 20 mL. The solutions were further diluted to obtain REE concentrations suitable for analysis. Finally, indium (In, 1 µg g^{-1}) was added in the final dilution as an internal standard (Spex Certiprep, USA) to minimize equipment fluctuations and matrix effects.

2.3. Rare earth element (REE) analyses

Samples were assessed for semi-total REE concentrations (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) and Y by ICP-MS (PerkinElmer NexIon 300D), following digestion by the USEPA 3051 A method. The determination was made by external calibration, and the analytical curve was constructed with 0.1, 0.5, 2, 10, and 20 µg kg^{-1}, in a 2 % nitric acid solution, from Spex standard solutions, containing 1000 µg kg^{-1} (Spex CertiPrep, USA) of individual REE isotopes: [89]Y,
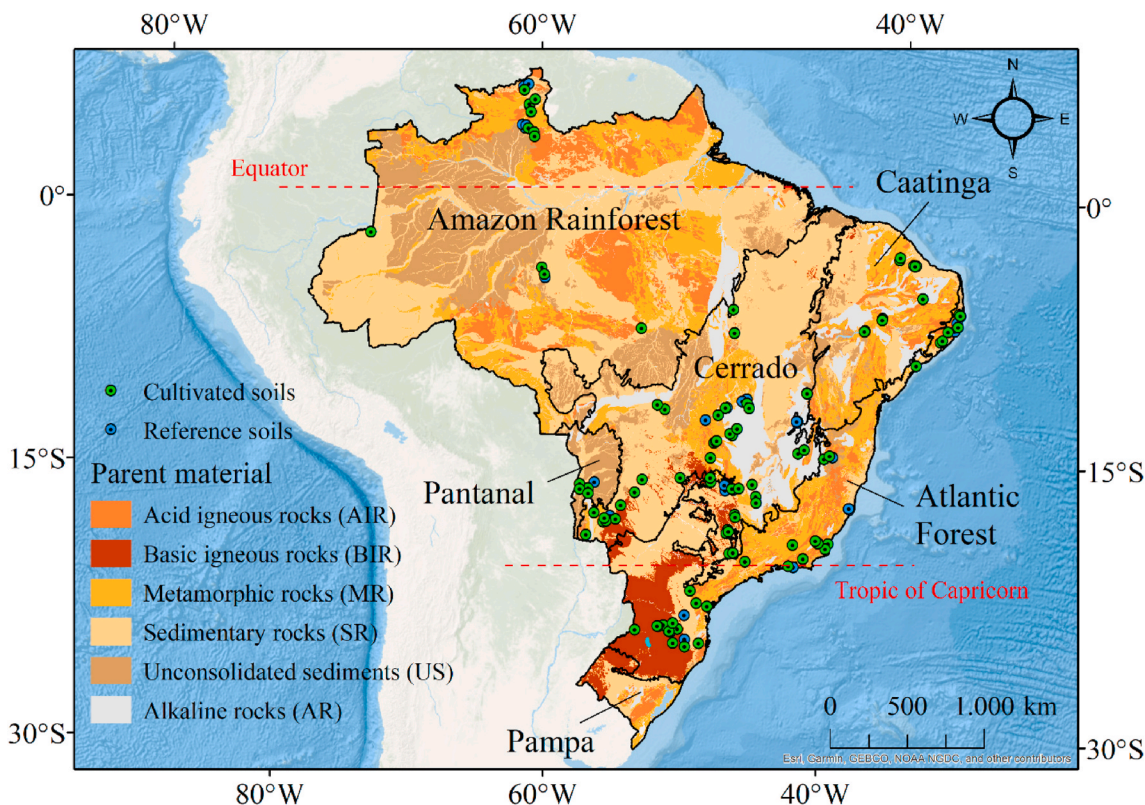
Fig. 1. Distribution of sampling sites from reference and cultivated soils in Brazil.

^{139}La, ^{140}Ce, ^{141}Pr, ^{142}Nd, ^{152}Sm, ^{153}Eu, ^{158}Gd, ^{159}Tb, ^{164}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{174}Yb, and ^{175}Lu. The operating conditions of the ICP-MS apparatus and the measurement parameters are presented in Table S2.

Analytical quality was controlled using a CRM (Calcareous Soil ERM-CC690®, Institute for Reference Materials and Measurements - IRMM, Belgium) in quadruplicate during the determination process to assess the accuracy of laboratory analyses (Table S3). The quantification limits (QL) were obtained after analyses of pentaplicate blank samples added to the analytical procedure. Since REE values were obtained by acid digestion (partial or leached contents - determined), we applied a correction factor on the partial analytical results (corrected) obtained by the USEPA 3051 A method to represent the total REE contents (recovery). Therefore, the measured REE concentrations in CRM ranged from 57 % (Tm) to 99.7 % (Nd). The highest recoveries were obtained for La, Nd, Sm, and Dy, while Ce, Gd, Tb, Tm, and Yb yielded the lowest recoveries. Results for quantification limits (QL) were ($\mu g\ kg^{-1}$): Y (0.69), La (0.72), Ce (0.72), Pr (0.79), Nd (0.80), Sm (0.83), Eu (0.87), Gd (0.89), Tb (0.91), Dy (0.91), Ho (0.94), Er (0.91), Tm (0.82), Yb (0.91), and Lu (0.93).

2.4. Traditional laboratory analyses

Each sample was air-dried and sieved to pass through a 2-mm nylon screen for all subsequent analyses. Soil chemical analyses were carried out following Brazilian standard procedures (Teixeira et al., 2017). Soil pH was determined in water with a potentiometer using a soil:solution ratio of 1:2.5 after shaking and 1-h rest. Organic Carbon (OC) was obtained by wet oxidation with potassium dichromate in sulfuric acid (Walkley and Black, 1934). Exchangeable cations (Ca^{2+}, Mg^{2+}, and Al^{3+}) were extracted with 1 mol L^{-1} KCl solution (McLean et al., 1958) and determined by a PerkinElmer atomic absorption spectrometer A Analyst 400. Available K and P were extracted by a Mehlich-l solution (0.0125 mol L^{-1} H_2SO_4 + 0.05 mol L^{-1} HCl) (Mehlich, 1953), with K being determined by flame photometer and P by colorimetry. Cation

exchange capacity [CEC = Ca^{2+} + Mg^{2+} + K^++ (H^+ + $Al3^+$)], base saturation (BS = Ca^{2+} + Mg^{2+} + K^+/T * 100), and aluminum saturation (m = Al^{3+} * 100/Ca^{2+} + Mg^{2+} + K^+ + Al^{3+}) were calculated from the aforementioned results.

Particle size distribution was analyzed according to Gee and Or (2002). Firstly, the sand fraction was separated using a 0.05-mm sieve; silt and clay fractions were then separated from each other after sedimentation of the silt fraction, by pipetting a volume of the solution containing only the clay fraction suspension. This solution was then oven-dried and the remaining clay fraction was weighted. The silt fraction quantification was obtained by subtracting the weights of sand and clay fractions from the total weight of the soil.

The major elements (expressed as oxides: Al_2O_3, Fe_2O_3, TiO_2, CaO, K_2O, P_2O_5, and MnO) concentrations were determined by portable X-ray fluorescence (pXRF) spectrometry, according to Weindorf and Chakraborty (2016), Silva et al. (2018b), and Silva et al. (2020). These measurements were carried out using a S1 Titan LE (Bruker Nano Analytics, Kennewick, WA, USA) X-ray spectrophotometer with Rh excitation tubes (operated at 4 W, 15–50 keV, and 5–100 μA) and a silicon drift detector with a resolution of <145 eV (based on pXRF calibration). The fluorescence detected was analyzed by the GeoChem software, after soil samples have been scanned during 60 s in triplicate, using the Trace (dual soil) mode. Samples certified by the National Institute of Standards and Technology (NIST 2709 A and 2710 A) and a check sample provided by pXRF manufacturer were used for quality assurance and control of equipment. The recovery percentages of the elements in CRMs are presented in Table S4. Only elements found above the limit of detection for all samples were considered.

2.5. Natural background and anthropogenic concentration determination for REE

The natural background concentrations (upper threshold) were defined as the natural REE concentrations in benchmark soils without

Table 1

Characteristics of soil databank concerning land use, soil type, biome, parent material, climate conditions, and type of native vegetation (number total of 175 soil samples). Individual 'n' in brackets.

Soil type[1]	Biome[2]	Parent material[3]	Köppen climatic class[4]	Native vegetation[5]
Reference (n = 68)				
Acrisols (7)	Amazon Rainforest (15)	Acid igneous rocks (6)	Af (2)	Caatinga 'white forest' (9)
Cambisols (14)	Atlantic Forest (19)	Basic igneous rocks (6)	Am (17)	Equatorial savanna (6)
Podzols (6)	Caatinga (11)	Alkaline rocks (11)	As (12)	Wetland (5)
Gleysols (3)	Cerrado (18)	Metamorphic rocks (13)	Aw (19)	Tropical field (9)
Ferralsols (16)	Pantanal (5)	Sedimentary rocks (9)	BSh (4)	Neotropical savanna (8)
Luvisols (1)		Unconsolidated sediments (23)	Cfb (6)	Equatorial rainforest (10)
Arenosols (6)			Cwb (8)	Ombrophilous forest (1)
Nitisols (2)				Tropical forest (20)
Histosols (1)				
Planosols (5)				
Plinthosols (4)				
Vertisols (3)				
Cultivated (n = 107)				
Acrisols (27)	Amazon Rainforest (9)	Acid igneous rocks (10)	Af (5)	Caatinga 'white forest' (19)
Cambisols (17)	Atlantic Forest (39)	Basic igneous rocks (12)	Am (18)	Wetland (2)
Gleysols (5)	Caatinga (13)	Alkaline rocks (7)	As (12)	Tropical field (3)
Ferralsols (38)	Cerrado (45)	Metamorphic rocks (19)	Aw (31)	Neotropical savanna (31)
Luvisols (1)	Pantanal (1)	Sedimentary rocks (28)	BSh (11)	Equatorial rainforest (5)
Arenosols (2)		Unconsolidated sediments (31)	Cfa (3)	Seasonal forest (2)
Nitisols (7)			Cfb (14)	Ombrophilous forest (5)
Histosols (2)			Cwa (6)	Tropical/ subtropical forest (40)
Planosols (1)			Cwb (7)	
Plinthosols (6)				
Vertisols (1)				

Source of information: [1]IUSS Working Group WRB (2014); [2]IBGE (2015); [3]This dataset; [4]Alvares et al. (2013); [5]IBGE (2015). Parent material: acid igneous rocks (granite, dacite) and plinthic sediments; basic igneous rocks (andesite with trachyte, basalt, gabbro-norite, melaphire); alkaline rocks (carbonate-pelitic, dolomite, limestone); metamorphic rocks (gneiss, gneiss-biotite, metasiltit, metashale, shale, slate, metabasite, migmatite, mica-schist, schist, micaceous gneiss, quartzite, calciferous quartzite, phyllite); sedimentary rocks (arcose, pelitic rocks, claystone, conglomerate, sandstone, siltstone, tuffite, sandy-clayey sediments); and unconsolidated sediments (detrital-lateritic cover, clay and sandy, alluvial, colluvial, and organic sediments).

anthropogenic influences (Matschullat et al., 2000; Reimann et al., 2005), and the anthropogenic concentrations are understood mainly as a sum of natural and anthropogenic sources of REE in cultivated soils. For the determination of the natural (geogenic) background and anthropogenic concentration, the equation proposed by Reimann et al. (2005) based on median and median absolute deviation (MAD) values was

calculated as follows:

Natural background or anthropogenic concentration (upper threshold) = Median + 2 MAD   (Eq.1)

Equation 1 is better suited for estimation of threshold values and the range of background data (Reimann et al., 2005; Rothwell and Cooke, 2015; Yotova et al., 2018).

2.6. Calculation of enrichment factors

The enrichment factors (EF) were calculated in order to differentiate the REE from anthropogenic and naturally occurring sources (Huang et al., 2019). The following formula was applied:

$$EF = \frac{[REE]sample/[REE]PAAS}{[Y]sample/[Y]PAAS} \qquad (Eq.2)$$

where REE and Y (yttrium) consist of elemental concentrations, and crust means the concentration of Post-Archean Australian Shale (PAAS) (Pourmand et al., 2012). Yttrium was considered as a reference due to its low mobility in several environment conditions (Huang et al., 2019). Thus, the contamination level of REE can be divided into six classes: non-enriched (EF < 1), slightly enriched (1 ≤ EF < 2), moderately enriched (2 ≤ EF < 5), significantly enriched (5 ≤ EF < 20), strongly enriched (20 ≤ EF < 40), and extremely enriched (EF ≥ 40) (Sutherland, 2000).

2.7. REE-normalized patterns, REE fractionation, and Ce and Eu anomalies

REE concentrations were normalized by logarithmic transformations of y-axis values containing Post-Archean Australian Shale (PAAS) as reported by Pourmand et al. (2012). Thus, this normalization was used to compare the REE concentrations linked to different parent materials and to identify possible contamination (Lin et al., 2013).

The La_N/Yb_N, La_N/Sm_N, Sm_N/Yb_N, and $LREE_N/HREE_N$ ratios were calculated, reflecting the fractionation of LREE and HREE used to interpret the geochemical REE patterns were calculated (Migaszewski et al., 2016, 2019), where N implies in normalized values. Cerium [δCe = Ce*/(0.5La*+0.5Pr*)] and Europium [δEu = Eu*/(Sm*. Dy*)/2] anomalies were calculated according to Bau and Dulski (1996), where La*, Ce*, Pr*, Sm*, Eu* and Dy* represent the REE contents in the PAAS-normalized (Pourmand et al., 2012). Values of δCe and δEu below 0.8 are indicative of negative anomalies whereas those above 1.2 point to positive anomalies (Grawunder et al., 2014; Migaszewski et al., 2016, 2019).

2.8. Statistical analyses

A priori, values below the detection limit (DL) were set to 1/2 DL. Consequently, all analytical data including REE from each site were square root transformed and standardized (Schucknecht et al., 2012) to address the data normality. Thus, these data were submitted to Pearson correlation analysis (α = 0.05) to understand the intercorrelations between soil physicochemical properties and REE concentrations. The Mann-Whitney test (α = 0.05) was performed in order to ascertain if there is statistical difference between REE concentration from reference and cultivated soil (Fig. 2).

Additionally, the median values and the median absolute deviation (MAD) compose the main parameter used to compare the geochemical data, since data distortion could affect the arithmetic mean values that do not adequately represent the natural contents of soil elements (Reimann et al., 2012). Boxplot analyses were also performed to display REE concentrations distribution in soils. The analytical results were organized according to the parent materials to generate more information about the effect of geological settings on REE concentrations. The
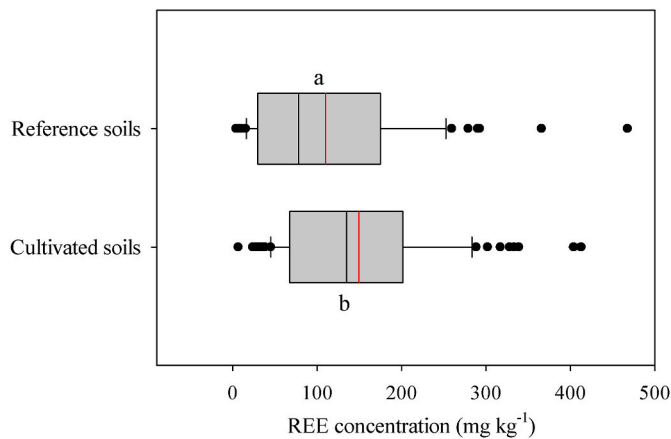
Fig. 2. Comparison of boxplots and outliers observed for REE concentrations in reference and cultivated soils. The mean and median are shown in redline and blackline, respectively. The letters indicate statistical significance by the Mann-Whitney test (α = 0.05).

descriptive statistics of soil properties associated to different parent materials are listed in Tables S5 and S6.

The effect of spatial data variability on the best model was tested in order to select the multiple linear regression method. Consequently, the GLS multiple linear regression and the exponential spatial correlation structure were used because the spatial component was relevant (correlation between the regression residues was found). In order to generate predictive models of REE (dependent variable) from GLS, LREE and HREE were fitted to the environmental explanatory variables: biomes, land use, soil types, parent material, sand content, and biome-land use interaction.

To build the models and make the predictions, the sand content was scaled - scaling for the data lie between a given minimum and maximum value - and the LREE and HREE concentrations from each location were square root transformed showing a data normality distribution:

standardized content = (x – mean(x))/std.dev(x), in which x is the original elemental LREE or HREE contents. The least important variables for model adjustment were removed after Analysis of variance (ANOVA) and Tukey's test to investigate statistically differences at α = 0.05 (Table S7 to S12 including Figures S1 and S2). The R software (R Development Core Team, 2018) and Sigma Plot 12.0 were used for the statistical analyses.

The models were ranked based on their AICc (Akaike information criteria corrected for small sample sizes) values, also used to assess models for the goodness of fit (Venables and Ripley, 2002). The lower AICc values (LREE: 417.0 and HREE: 424.3) indicated better models that demonstrated data spatial dependence after modeling by GLS and exponential spatial correlation structure. Additionally, the variation of **Δ**AICc with respect to the best model (the smallest AIC) and to each model (so the best model has a **Δ**AICc of zero) and the Akaike weight (Wt) showing the relative likelihood for each model (LREE: 0.64 and HREE: 0.91) are presented in Table 2.

3. Results and discussion

3.1. Multiple regression analysis – predictive models

The summary results of GLS multiple linear regression models for predicting semi-total concentrations of LREE (La to Eu) and HREE (Gd to Lu) are presented in Table 2. Additional tables and figures of the statistical analyses are shown in the Supplementary material.

The explanatory variables (biomes, land use, and sand fraction content) were statistically significant (Tukey's test, α = 0.05), showing predictive power for both LREE and HREE contents among the variables analyzed (Supplementary material). However, the inclusion of soil parent material resulted in the best prediction model of HREE contents (besides biomes, land use, and sand fraction content), and is noteworthy.

The Caatinga biome was statistically different from the Amazon Rainforest and Cerrado biomes for LREE contents and from Amazon Rainforest for HREE contents. The Caatinga biome is predominant in the semi-arid Brazilian region, and unlike other biomes, there is a strongly

Table 2

Summary of multiple regression models for the semi-total content of light (LREE) and heavy rare earth elements (HREE) (response variables), showing the explanatory variables in each model, the Akaike information criteria corrected for small sample sizes (AIC$_c$), the variation of AIC$_c$ with respect to the best model (ΔAIC$_c$), and the Akaike weight for each model (Wt).

Response variable	Model[a]	Explanatory Variables[b]						AIC$_c$[c]	ΔAIC$_c$	Wt
		Biome	Parent material	Soil type	Land use	Sand fraction	Biome-Land use			
LREE content	1	X			X	X		417.0	0	0.64
	2	X			X			419.0	2	0.24
	3	X		X	X	X		420.5	3.5	0.11
	4				X			425.7	8.6	0.01
	5	X						426.4	9.4	0.01
	6	X		X	X	X		431.7	14.7	0.00
	7							436.0	19.0	0.00
	8	X	X	X	X	X	X	446.0	28.9	0.00
	9	X	X	X	X	X		449.6	32.5	0.00
HREE content	1	X	X		X	X		424.3	0	0.91
	2	X			X	X		429.9	5.7	0.05
	3	X	X	X	X	X	X	432.6	8.3	0.01
	4	X		X	X	X		433.4	9.1	0.01
	5	X			X			433.9	9.6	0.01
	6				X			436.5	12.2	0.00
	7	X	X	X	X	X		436.9	12.6	0.00
	8	X			X			437.0	12.7	0.00
	9							442.4	18.1	0.00

AIC$_c$ (Akaike information criteria corrected for small sample sizes); ΔAIC$_c$ (the variation of AIC$_c$ with respect to the best model); and Wt (Akaike weight for each model).

[a] Models were ranked based on AIC$_c$ values and the best model for each response variable (LREE and HREE) is showed in first model.

[b] For each model (rows) the crosses indicate the respective explanatory variable (biome, parent material, soil type, land use - reference or cultivated, sand fraction content, and the biome-land use interaction) is included in the model. The explanatory variables (biome, parent material, land use, and sand fraction content) were statistically significant (Tukey's test, α = 0.05).

[c] Lower values of AIC$_c$ indicate the better models.

negative atmospheric water balance (average precipitation below 900 mm year^{-1} and potential evapotranspiration above 2200 mm year^{-1}) (Pinheiro et al., 2016). This condition leads to a less intense soil weathering-leaching, where the environment is more conservative of REE (evapotranspiration > precipitation water balance) (Arruda et al., 2017; Menezes et al., 2020), and is usually a situation occurring in locations known for having the main REE reserves in Brazil (Antoniassi et al., 2015; Neumann and Medeiros, 2015; Ramos et al., 2016a). Unlike the Caatinga, which is a biome conservative of REE, the Amazon Rainforest (humid tropical climate) and the Cerrado (tropical climate) biomes have soils that are highly weathered-leached, which causes a greater depletion of REE.

In particular, in the Amazon Rainforest biome there is a change in the pedoenvironment through the strong interaction between the biota-soil system, which are also influenced by abiotic factors - climate and parent material (Zaharescu et al., 2017; Souza et al., 2018; Ferreira et al., 2021). Such conditions allow the dissolution of REE-rich minerals and the mobilization for aqueous solution due to the intense chemical weathering.

Higher REE contents were found in cultivated soils (from 6.7 to 413 mg kg^{-1}, with a median value of 135 mg kg^{-1}). The REE concentrations varied from 4.0 to 467.7 mg kg^{-1} in reference soils, with a median value of 78 mg kg^{-1}. In Fig. 2, the boxplots comparing the REE concentrations from cultivated and reference soils clearly show the significant difference between the two groups for LREE and HREE contents, confirmed by Mann-Whitney test (p = 0.002).

This difference in the median values of cultivated soils compared with reference soils indicates an increase in REE contents. This is possibly influenced by the intensive application of products from the phosphate industry (e.g., P fertilizers and phosphogypsum) (Lopes and Guilherme, 2016; Withers et al., 2018) containing REE (Hu et al., 2006; Ramos et al., 2016a, 2016b; Silva et al., 2019) in cultivated soils. In general, the sand fraction of Brazilian soils is composed mainly of

quartz. Although quartz does not contain REE (Vermeire et al., 2016), it was relevant for the prediction of LREE and HREE contents due to its performance as a diluent in soils (Hardy and Cornu, 2006).

A clear effect of the parent material was observed solely on the prediction model of HREE contents in topsoil, especially in soils closely linked to different REE-bearing minerals (probably xenotime, monazite, apatite, aluminum phosphate sulfate, etc.) originated from acid and basic igneous rocks, and alkaline rocks that did not statistically differ. Most of HREE included in soils developed from these parent materials is not expected to be highly mobilized during pedogenesis (Laveuf and Cornu, 2009), and consequently reflects the composition mineralogical of parent material.

The decreasing order of total REE contents in the following rocks from Brazil was registered by Sá Paye et al. (2016): alkaline rocks > sedimentary rocks > unconsolidated clay sediments > metamorphic rocks > basic igneous rocks > unconsolidated sand and silt sediments > acid igneous rocks. Thus, such order should be considered when assessing REE contents in Brazilian soils, taking into account that the parent material is the alteration product of the bedrock and the soil is the product of alteration of the parent material, through pedogenic processes. Theses aspects place emphasis on the common scenario in Brazil and in many conceivable Latin American countries, where these explanatory variables (biomes, land use, sand fraction content, along with parent materials) could function as environmental indicators for predicting REE in soils.

3.2. Natural background concentration of REE in reference soils

Table 3 compares the results of REE concentration in reference topsoils - i.e., natural background concentrations (NBC) - from different parent materials. Considering that the NBC may change from area to area, these values could guide and regulate the limits considering the natural characteristics, subsidizing regulatory policies in a more realistic

Table 3

Median, median absolute deviation (MAD) and natural background concentration (upper threshold, Median+2 MAD) of rare earth elements from reference soils (in mg kg^{-1}). Calculated ratios, anomalies and fractionation indices for the studied samples are also presented.

	Acid igneous rocks		Basic igneous rocks		Alkaline rocks		Metamorphic rocks		Sedimentary rocks		Unconsolidated sediments	
	Median ±MAD	Median +2 MAD	Median ±MAD	Median +2 MAD	Median ±MAD	Median +2 MAD	Median ±MAD	Median +2 MAD	Median ±MAD	Median +2 MAD	Median ±MAD	Median +2 MAD
	mg kg^{-1}											
Y	4.7 ± 2.5	9.7	12.9 ± 9.8	32.5	26.5 ± 13	52	7.5 ± 9	25.5	4.2 ± 2	8.2	2.0 ± 2.1	6.2
La	17.5 ± 4.4	26.3	16.8 ± 22	60.4	49 ± 8.7	66.4	31 ± 20	70.4	14.5 ± 8.2	30.9	7.4 ± 7.2	21.8
Ce	22.3 ± 2.8	27.9	31.8 ± 38	107	65 ± 14	93.2	47 ± 30	107	20 ± 18	55.4	14.5 ± 12	39.5
Pr	3.0 ± 0.7	4.4	3.2 ± 4.2	11.6	10 ± 2.8	16	6.4 ± 2.8	12	2.5 ± 1.8	6.1	1.1 ± 0.9	2.9
Nd	15.9 ± 5.5	26.9	22 ± 27	76.8	63 ± 23	108	37 ± 20	76.6	14.3 ± 13	40.3	7.0 ± 6	19
Sm	1.5 ± 0.6	2.7	2.4 ± 2.9	8.2	5.6 ± 2	9.6	3.2 ± 1.7	6.6	1.5 ± 1.1	3.7	0.5 ± 0.6	1.7
Eu	0.4 ± 0.2	0.8	0.7 ± 0.8	2.3	1.2 ± 0.8	2.8	0.5 ± 0.4	1.3	0.2 ± 0.2	0.6	0.2 ± 0.04	0.3
Gd	1.1 ± 0.5	2.1	1.8 ± 2.1	6	4.0 ± 2	8	2.6 ± 1.6	5.8	1.1 ± 0.9	2.9	0.3 ± 0.1	0.5
Tb	0.2 ± 0.1	0.4	0.4 ± 0.4	1.2	0.7 ± 0.6	1.9	0.3 ± 0.2	0.7	0.2 ± 0.05	0.3	0.2 ± 0	0.2
Dy	1.1 ± 0.6	2.3	2.7 ± 2.4	7.5	5.2 ± 2.4	10	2.5 ± 2.5	7.5	0.9 ± 0.7	2.3	0.4 ± 0.2	0.8
Ho	0.1 ± 0.06	0.2	0.34 ± 0.3	0.94	0.5 ± 0.5	1.5	0.2 ± 0.2	0.6	0.2 ± 0.1	0.4	0.2 ± 0	0.2
Er	0.4 ± 0.2	0.8	0.9 ± 1	2.9	1.6 ± 0.9	3.4	0.6 ± 0.6	1.8	0.3 ± 0.1	0.5	0.2 ± 0.1	0.4
Tm	0.04 ± 0.02	0.1	0.2 ± 0.04	0.28	0.2 ± 0.1	0.4	0.1 ± 0.12	0.34	0.1 ± 0.05	0.2	0.2 ± 0	0.2
Yb	0.4 ± 0.2	0.8	1.2 ± 1.2	3.6	1.9 ± 1	3.9	0.6 ± 0.5	1.6	0.3 ± 0.1	0.52	0.2 ± 0.1	0.4
Lu	0.04 ± 0.02	0.1	0.2 ± 0.05	0.34	0.2 ± 0.001	0.2	0.1 ± 0.1	0.3	0.1 ± 0.05	0.2	0.2 ± 0	0.2
LREE	61 ± 13	92	77 ± 99	276	194 ± 58	304.8	125 ± 65	256	53 ± 50	154	31 ± 24	78.4
HREE	3.4 ± 1.6	6.6	7.8 ± 5.7	18.7	14.3 ± 7	26.5	7 ± 6.7	20.5	3.2 ± 2.2	8	1.9 ± 0.7	3.3
REE	64 ± 16	102.8	85 ± 105	295	208 ± 70	343.5	132 ± 70	274	56.2 ± 54	163	33 ± 25	82
δCe	0.7		1.0		0.7		0.8		0.8		1.2	
δEu	1.6		1.3		1.1		0.9		0.9		2.2	
La$_N$/Yb$_N$	3.0		0.9		1.7		3.5		3.3		2.5	
La$_N$/Sm$_N$	1.8		1.1		1.4		1.5		1.5		2.3	
Sm$_N$/Yb$_N$	1.6		0.9		1.3		2.3		2.2		1.1	
LREE$_N$/ HREE$_N$	1.9		1.1		1.5		1.9		1.8		1.7	

LREE (La to Eu), HREE (Gd to Lu), and REE (La to Lu); δCe = Ce$_N$/(0.5La$_N$.0.5Pr$_N$) and δEu = Eu$_N$/(Sm$_N$.Dy$_N$)/2; where N implies in normalized values by Post-Archean Australian Shale (PAAS) (Pourmand et al., 2012).

manner. In general, the individual NBC followed the order: Ce > Nd > La > Y > Pr > Sm > Dy > Gd > Yb = Er > Eu > Tb > Ho > Tm > Lu, being similar to the sequence found in the earth's crust (Rudnick and Gao, 2014; Cunha et al., 2018; Silva et al., 2018a). Especially in reference soils (natural), REE contents are inherited from the easily-weatherable primary minerals bearing these elements and their maintenance in the soil systems (Lijun et al., 2004).

The reference soils derived from alkaline rocks presented the highest NBC for most of the REE followed by basic igneous rocks, metamorphic rocks, sedimentary rocks, acid igneous rocks, and unconsolidated sediments. This comparative REE-enrichment in soils originated from alkaline rocks is due to occurrence of hydroxide complexes in such environments as well as to the presence of REE-rich minerals that are resistant to weathering (Chen and Yang, 2010; Sadeghi et al., 2013b; Sá Paye et al., 2016).

The main REE reserves in Brazil occur in association with alkali-carbonatitic complexes (Antoniassi et al., 2015; Neumann and Medeiros, 2015; Ramos et al., 2016a), mainly in the Caatinga biome. Hence, the higher REE concentrations were found in soils originated from alkaline rocks that are under alkaline conditions (median pH value of 6.7, in Table S5), which render the low solubility of REE (Chen and Yang, 2010; Han et al., 2017; Mihajlovic and Rinklebe, 2018). In this manner, REE are also rapidly adsorbed and relatively immobilized on soil colloidal materials or organic matter (Bao and Zhao, 2008; Mihajlovic and Rinklebe, 2018; Silva et al., 2018a; Dinali et al., 2019), due to their predominant negative charges (Tyler, 2004).

Conversely, reference soils originated from acid igneous rocks, sedimentary rocks, and unconsolidated sediments revealed the lower NBC because of the smaller REE concentrations on parent materials (Table 3) This confirms the strong influence of parent materials and soil-forming factors on REE distribution in soils, yet there may be also an influence of soil particle size distribution, organic matter, clay mineralogy, and rock-microorganism-plant interactions (Han et al., 2017; Zaharescu et al., 2017; Dinali et al., 2019).

The NBC of this study were slightly lower than the values reported by Rudnick and Gao (2014) and Sá Paye et al. (2016). Conversely, the NBC values were higher than those reported for selected soils from Brazil (Licht et al., 2006; Silva et al., 2016, 2018a), Cuba (Alfaro et al., 2018), Japan (Yoshida et al., 1998), Sweden (Sadeghi et al., 2013a), Europe (Sadeghi et al., 2013b), and China (CNEMC, 1990).

In Table 3, the individual La_N/Yb_N, La_N/Sm_N, Sm_N/Yb_N, and $LREE_N/HREE_N$ ratios were calculated to measure the degree of REE fractionation that would confirm a LREE enrichment compared with that of MREE and HREE, which is typical of soils originated on alkaline and sedimentary rocks (Chen and Yang, 2010; Dołęgowska and Migaszewski, 2013). Conversely, soils developed from basic igneous rocks presented HREE enrichment as showed by La_N/Yb_N (0.9) and Sm_N/Yb_N (0.9) ratios, possibly due to substantial contents of minerals containing HREE as "impurities" (Kanazawa and Kamitani, 2006; Laveuf and Cornu, 2009), because these minerals are not expected to be highly mobilized during pedogenesis.

Cerium, is the lightest and the most abundant REE in soils probably due to its incorporation into clay minerals structures, Fe-, Mn- and Al-oxyhydroxides, and organic matter in its oxidized form Ce(IV), which has the smallest ionic radius (Cao et al., 2001; Laveuf and Cornu, 2009). Although with slightly negative Ce anomalies (δCe <0.8), Ce depletion was found in soils developed from different parent materials (acid igneous rocks and alkaline rocks) when compared with La and Pr (Table 3). Conversely, positive Eu anomalies in soils developed from acid igneous rocks, basic igneous rocks, and unconsolidated sediments indicated an Eu enrichment when compared with Sm and Gd.

3.3. Anthropogenic concentration of REE in cultivated soils

The median REE concentrations, as well as anthropogenic REE concentrations in cultivated soils developed from different parent materials are presented in Table 4, being higher than NBC in reference soils. Besides, the anthropogenic REE concentrations decrease in the following sequence (mg kg^{-1}): acid igneous rocks (407.4) > metamorphic rocks (351.2) > basic igneous rocks (302) > alkaline rocks (295) > unconsolidated sediments (277) > sedimentary rocks (214.5), being the values higher than those obtained in agricultural soils from Europe and Sweden (Sadeghi et al., 2013a) and soils form the GEMAS project (Reimann et al., 2014). These findings indicate that an intense agricultural activity in Brazil, with a long-term use of phosphate inputs, could be facilitating REE mineralization.

The La_N/Yb_N, La_N/Sm_N, Sm_N/Yb_N, and $LREE_N/HREE_N$ ratios values evidenced LREE and MREE enrichments compared with HREE in cultivated soils originated from the studied parent materials. During chemical weathering, Ce tends to behave differently from other REE (Bao and Zhao, 2008), occurring in trivalent and tetravalent valences states in soils. Therefore, the positive Ce anomaly observed in soils developed from basic igneous rocks and sedimentary rocks were consequences of the oxidation of Ce(III) to Ce(IV), which becomes insoluble as cerianite (CeO_2) in oxidizing environments via adsorption on Fe- and Mn-hydroxides (Vázquez-Ortega et al., 2015; Chang et al., 2016). Thus, Ce remained in the surface soils while other REE were leached away. Europium deviates from other REE in that it occurs in both trivalent and divalent valences states. Therefore, a positive Eu anomaly predominates in most rocks and soils.

3.4. Soil contamination assessment

One of the main hypotheses of this study was that phosphate products application would increase REE in Brazilian soils. To investigate the potential soil contamination with REE, REE-normalized patterns (Figures S3 and S4), REE fractionation indices (La_N/Yb_N, La_N/Sm_N, Sm_N/Yb_N, and $LREE_N/HREE_N$ ratios) and geochemical anomalies ratios (δCe and δEu) (Tables 3 and 4), as well as enrichment factors - EF (Table 5) were calculated. We also used natural background concentrations as a reference to detect soils contaminated by REE as reported by Galuszka et al. (2007) and Díez et al. (2007).

In past decades, high inputs of phosphate fertilizers were used for increasing agricultural yields in Brazil (Turra et al., 2011; Lopes and Guilherme, 2016; Withers et al., 2018; Zhou et al., 2018), with many of those being commonly enriched in REE (Ramos et al., 2016a; Cunha et al., 2018). Irrespectively of the fact that P fertilizers marketed in Brazil present a wide variety of REE contents depending on the raw material used (mostly carbonatite, igneous, meta-sedimentary, and lateritic rocks from the Precambrian age) and the rock processing operations, as demonstrated by Ramos et al. (2016a, 2016b), evidences of REE enrichment were observed in cultivated soils, as is discussed further.

The REE-normalized patterns in reference and cultivated soils from different parent materials are shown in Figures S3 and S4, respectively. As a whole, the REE-normalized patterns in cultivated soils developed from acid and basic igneous rocks, metamorphic rocks, sedimentary rocks, and unconsolidated sediments were mainly characterized by LREE-MREE enrichment. However, this same enrichment in soils originated from alkaline rocks was not clearly observed. The results suggest that regardless of land use, soils originated from alkaline rocks tend to be enriched in REE (Sá Paye et al., 2016; Alfaro et al., 2018). Under such conditions, the REEs may be adsorbed by residuum after chemical weathering of carbonate rocks or carbonatites (mixture of clay minerals and Fe- and Mn-hydroxides), or these soils may contain pieces of REE-bearing carbonatites (as evidenced by positive correlations between REE and Ca/Mg).

This enrichment found in REE-normalized patterns helps to understand the influence of anthropogenic activities on the distribution of LREE-MREE in diverse geopedologic contexts and may be related to REE adsorption by Fe- and Mn-hydroxides minerals, clay minerals, or organic matter in soils (Palumbo et al., 2001; Zhang and Shan, 2001), in

Table 4

Median, median absolute deviation (MAD) and anthropogenic concentration (upper threshold, Median+2 MAD) of rare earth elements from cultivated soils (in mg kg^{-1}). Calculated ratios, anomalies and fractionation indices for the studied samples are also presented.

	Acid igneous rocks		Basic igneous rocks		Alkaline rocks		Metamorphic rocks		Sedimentary rocks		Unconsolidated sediments	
	Median ±MAD	Median +2 MAD	Median ±MAD	Median +2 MAD	Median ±MAD	Median +2 MAD	Median ±MAD	Median +2 MAD	Median ±MAD	Median +2 MAD	Median ±MAD	Median +2 MAD
	mg kg^{-1}											
Y	18.4 ± 11	39.7	17.2 ± 11	38.5	17 ± 8.2	33.6	7.3 ± 7.9	23.2	4.7 ± 1.9	8.5	11 ± 12	34.9
La	60 ± 19	98.7	23.7 ± 16	56	44.3 ± 9	62.4	25 ± 26	76.8	15.7 ± 9	33.7	27 ± 20	66.3
Ce	84.8 ± 61	207	62 ± 23.5	109	55 ± 22.5	100	46 ± 41.9	129	36.5 ± 27	90.5	34 ± 35	103.4
Pr	11.6 ± 3.9	19.3	5.4 ± 3.2	11.7	8.5 ± 2.6	13.7	5.0 ± 5.4	15.7	3.1 ± 1.9	7.0	4.1 ± 4.3	12.7
Nd	82 ± 32.5	146	38 ± 21.2	80.6	58 ± 12.4	82.6	30 ± 34.4	98.9	19.8 ± 13	45	28 ± 23	74.7
Sm	6.3 ± 3.3	13	4.0 ± 1.9	7.9	5.1 ± 1.3	7.8	3.0 ± 3.6	10.1	1.7 ± 1.2	4.0	3.2 ± 2.8	8.9
Eu	1.3 ± 0.8	2.9	1.0 ± 0.6	2.3	1.1 ± 0.2	1.5	0.4 ± 0.2	0.83	0.3 ± 0.1	0.6	0.5 ± 0.5	1.4
Gd	4.6 ± 1.8	8.3	3.0 ± 1.3	5.7	3.5 ± 0.9	5.3	2.2 ± 2.7	7.7	1.2 ± 0.8	2.7	2.2 ± 2.4	7.0
Tb	0.6 ± 0.2	1.0	0.4 ± 0.3	1.0	0.5 ± 0.2	0.97	0.2 ± 0.1	0.4	0.2 ± 0.1	0.5	0.2 ± 0.2	0.7
Dy	5.7 ± 1.7	9.2	3.7 ± 2.3	8.3	4.3 ± 1.3	6.8	1.9 ± 2.2	6.2	1.3 ± 1.0	3.3	2.2 ± 2.5	7.2
Ho	0.2 ± 0.21	0.6	0.3 ± 0.2	0.6	0.3 ± 0.1	0.5	0.2 ± 0.06	0.4	0.2 ± 0.05	0.3	0.2 ± 0	0.2
Er	1.4 ± 0.45	2.3	1.3 ± 0.7	2.7	1.4 ± 0.3	2.0	0.4 ± 0.2	0.9	0.3 ± 0.1	0.5	0.5 ± 0.6	1.6
Tm	0.21 ± 0	0.21	0.2 ± 0	0.2	0.2 ± 0	0.2	0.2 ± 0	0.2	0.2 ± 0	0.2	0.2 ± 0	0.2
Yb	1.6 ± 0.9	3.4	1.4 ± 0.7	2.8	1.5 ± 0.4	2.2	0.4 ± 0.3	1.1	0.3 ± 0.1	0.6	0.4 ± 0.5	1.5
Lu	0.24 ± 0	0.24	0.24 ± 0	0.24	0.24 ± 0	0.24	0.24 ± 0	0.24	0.24 ± 0	0.2	0.24 ± 0	0.2
LREE	246 ± 68	373	134 ± 72	284	172 ± 57	277	109 ± 109	340.7	77 ± 59	204.8	97 ± 80	274
HREE	14.5 ± 4.9	24	10.5 ± 4.6	19	11.9 ± 3	17.9	5.7 ± 5.3	16.3	3.9 ± 1.9	7.6	6.1 ± 6	18.4
REE	260 ± 76.4	407.4	145 ± 75	302	184 ± 60	295	115 ± 113	351.2	81 ± 61.4	214.5	103 ± 80	277
δCe	0.8		1.3		0.7		1.0		1.3		0.8	
δEu	1.1		1.3		1.2		0.8		1.0		0.9	
La$_N$/Yb$_N$	2.5		1.1		2.0		4.2		3.5		4.5	
La$_N$/Sm$_N$	1.5		0.9		1.3		1.3		1.4		1.3	
Sm$_N$/Yb$_N$	1.7		1.3		1.5		3.3		2.5		3.5	
LREE$_N$/HREE$_N$	1.8		1.4		1.6		2.0		2.1		1.7	

LREE (La to Eu), HREE (Gd to Lu), and REE (La to Lu); δCe = Ce$_N$/(0.5La$_N$.0.5Pr$_N$) and δEu = Eu$_N$/(Sm$_N$.Dy$_N$)/2; where N implies in normalized values by Post-Archean Australian Shale (PAAS) (Pourmand et al., 2012).

Table 5

Enrichment factor for rare earth element (REE) concentrations from reference and cultivated soils.

REE	Acid igneous rocks		Basic igneous rocks		Alkaline rocks		Metamorphic rocks		Sedimentary rocks		Unconsolidated sediments	
	Ref. $n = 6$	Cult. $n = 10$	Ref. $n = 6$	Cult. $n = 12$	Ref. $n = 11$	Cult. $n = 7$	Ref. $n = 13$	Cult. $n = 19$	Ref. $n = 9$	Cult. $n = 28$	Ref. $n = 23$	Cult. $n = 31$
La	2.3	7.8	0.8	1.1	1.1	1.0	2.5	2.0	2.1	2.3	2.3	8.2
Ce	1.5	5.6	0.8	1.5	0.8	0.6	1.9	1.9	1.5	2.7	2.2	5.2
Pr	1.7	6.6	0.7	1.1	1.1	0.9	2.3	1.8	1.6	2.0	1.5	5.5
Nd	2.5	12.7	1.3	2.2	1.7	1.6	3.6	2.9	2.5	3.4	2.6	10.2
Sm	1.3	5.3	0.7	1.2	0.8	0.8	1.7	1.6	1.4	1.6	1.0	6.4
Eu	1.9	6.2	1.2	1.8	1.1	0.9	1.5	1.1	1.2	1.6	2.5	5.4
Gd	1.1	4.4	0.6	1.1	0.7	0.6	1.6	1.3	1.2	1.3	0.7	5.0
Tb	1.3	3.7	0.9	0.9	0.9	0.6	1.1	1.0	1.8	1.8	3.7	3.7
Dy	1.2	6.2	1.1	1.5	1.0	0.8	1.7	1.3	1.1	1.6	1.0	5.7
Ho	0.7	1.1	0.7	0.6	0.5	0.3	0.8	0.8	1.1	1.5	3.1	3.1
Er	0.7	2.6	0.6	0.9	0.5	0.5	0.7	0.4	0.6	0.6	1.0	2.0
Tm	0.5	2.7	1.0	1.0	0.5	0.5	0.9	1.7	0.9	3.0	6.4	6.4
Yb	0.8	3.2	0.8	1.0	0.7	0.5	0.7	0.5	0.7	0.7	1.0	2.0
Lu	0.5	3.2	1.2	1.2	0.6	0.6	0.8	2.0	0.8	3.6	7.5	7.5
LREE	17.3	70.1	8.0	14	9.8	8.7	22.4	19.5	16.9	24.6	20.6	64.7
HREE	2.4	10.5	2.1	2.8	1.9	1.5	3.2	2.6	2.6	3.3	3.6	10.7
REE	1.8	7.2	0.9	1.5	1.0	0.9	2.3	2.0	1.7	2.5	2.1	6.7

Ref.: reference soil; Cult.: cultivated soil; n: number of samples; LREE (La to Eu), HREE (Gd to Lu), and REE (La to Lu). The contamination level of REE can be divided into six classes: non-enriched (EF < 1), slightly enriched (1 ≤ EF < 2), moderately enriched (2 ≤ EF < 5), significantly enriched (5 ≤ EF < 20), strongly enriched (20 ≤ EF < 40), and extremely enriched (EF ≥ 40) (Sutherland, 2000).

association to their consequent low mobility (Xinde et al., 2000). Most tropical soils have significant amounts of such Fe-, Mn- and Al-oxyhydroxides (Laveuf and Cornu, 2009; Ling et al., 2015; Dinali et al., 2019) and present acidic pH conditions making them effectives as carriers of REE. Thus, the process of formation of rocks influenced by the thermodynamic nature of each element can control REE fractionation and REE signatures varied for different parent materials, showing the importance of the mineralogical composition to predict REE-rich pedoenvironments.

According to Table 5, remarkable LREE enrichments - i.e., extremely enriched soils - were observed in cultivated soils developed from acid igneous rocks and unconsolidated sediments (EF: 70.1 and 64.7, respectively). In cultivated soils derived from sedimentary rocks, there was a strong LREE enrichment (EF: 24.6), and in soils formed from basic igneous and metamorphic rocks there was a significant LREE enrichment (EF: 14 and 19.5, respectively). Unlike the others, cultivated soils

originated from alkaline rocks did not present LREE enrichment, possibly due to the high natural REE background concentration. The fractionation indices (La_N/Yb_N and Sm_N/Yb_N ratios) in cultivated soils developed from metamorphic rocks (4.2 and 3.3), sedimentary rocks (3.5 and 2.5), and unconsolidated sediments (4.5 and 3.5) revealed a significant LREE and MREE enrichment when compared with HREE. The evidence of enrichment was not clear for Ce and Eu anomalies.

The composition of soil parent material is one of the main drivers of soil-REE variability considering the natural concentrations. However, because of human activities such as the application of REE-rich agricultural inputs (e.g., P fertilizers and phosphogypsum) (Ramos et al., 2016a), REE enrichment would be expected. As is possible to notice in multiple regression analyses (Table 2), the land use influenced the accumulation of REE in cultivated soils. Hence, LREE and HREE contents in cultivated soils were statistically different and greater than in reference soils. For this reason, these results revealed that the REE accumulation in cultivated soils originated primarily from anthropogenic sources such as the long-term use of phosphate products.

3.5. Correlation analyses

The individual REE concentrations are mainly related to soil granulometry and physicochemical properties (Sá Paye et al., 2016), which in turn are influenced by parent materials, soil mineralogy, pedogenic processes, and soil types. In this sense, the summary of the Pearson's correlation matrix revealed the intercorrelations between soil-REE concentrations and soil attributes (Figs. 3 and 4). In general, REE in reference soils presented significant statistical correlation ($p < 0.05$) with clay fraction content, pH, CEC, exchangeable cations (K^+, and $Ca^{2+} + Mg^{2+}$), and oxides (Fe_2O_3, MnO, K_2O, and CaO) (Fig. 3), corroborating some authors (Tyler, 2004; Hu et al., 2006; Sá Paye et al., 2016; Alfaro et al., 2018; Dinali et al., 2019). Furthermore, the clay fraction content, OC, and Fe_2O_3 had a strong influence on CEC in topsoil, which in turn helps retaining REE in the soil.

Even though one could expect a significant correlation between REE and OC (Sá Paye et al., 2016; Vermeire et al., 2016; Silva et al., 2017), this was not found in our study ($p < 0.05$), which may be explained by
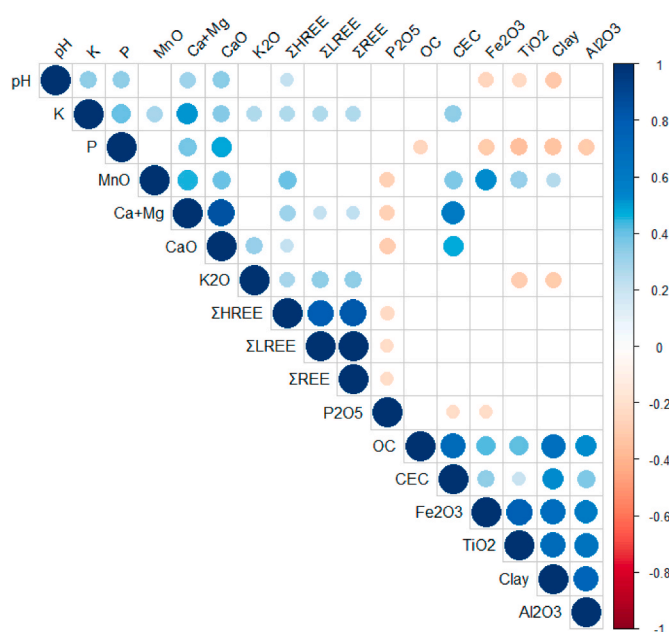

Fig. 4. Pearson's correlations matrix among REE, soil texture, and physicochemical properties ($p < 0.05$) in cultivated soils ($n = 94$). Positive correlations are displayed in blue and negative correlations in red color. Color intensity and the size of the circle are proportional to the correlation coefficients. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

the possible differential composition, stability, and characteristics of OC compounds found in these various tropical soils environments (Resende et al., 2014).

REE adsorption is favored by alkaline conditions (i.e., soil pH, which is linked to $Ca^{2+} + Mg^{2+}$ contents) and high CEC (Coppin et al., 2002; Dinali et al., 2019), yet alkaline conditions do not point to REE adsorption by carbonate minerals. Thus, acidic soils adsorb REE mostly as outer-sphere complexes in basal surfaces. Conversely in alkaline soils, the adsorption as inner-sphere complexes may occur at the edges of the colloidal particles (Cao et al., 2001; Coppin et al., 2002), which thus make REE more strongly retained in soils. Finally, REE retention is also increased by the higher CEC of soils and Fe- and Mn-hydroxides contents as reported by Tyler (2004), Laveuf and Cornu (2009), and Sá Paye et al. (2016).

Significant correlations were found for REE and $Ca^{2+} + Mg^{2+}$ and K^+ contents due to similar electronegativity of REE and Ca (Laveuf and Cornu, 2009), which favors Ca substitution into mineral structures by REE (Kanazawa and Kamitani, 2006). These findings indicate that the chosen chemical attributes in topsoil, including cations ($Ca^{2+} + Mg^{2+}$ and K^+) explained part of the variation found between soil properties and partial REE contents.

In cultivated soils, REE presented weak significant statistical correlation ($p < 0.05$) with K_2O, K^+, and CaO (Fig. 4). In this study, we did not find a significant correlation between REE and P_2O_5, which might be related to the high diversity of REE contents in phosphate products used in Brazilian agriculture, as observed by Ramos et al. (2016a). The REE contents in P-fertilizers vary widely, which leads to varied effects of their additions on agricultural soils. Because farmers may use fertilizers from different sources (e.g., sedimentary rocks - with smaller and less soluble REE compounds - or igneous rocks - with higher and more soluble REE compounds) (Ramos et al., 2016a), the differences of REE distribution patterns in soils receiving similar quantities o P fertilizers is certainly related to particularities of the different fertilizers that are applied in agroecosystems.
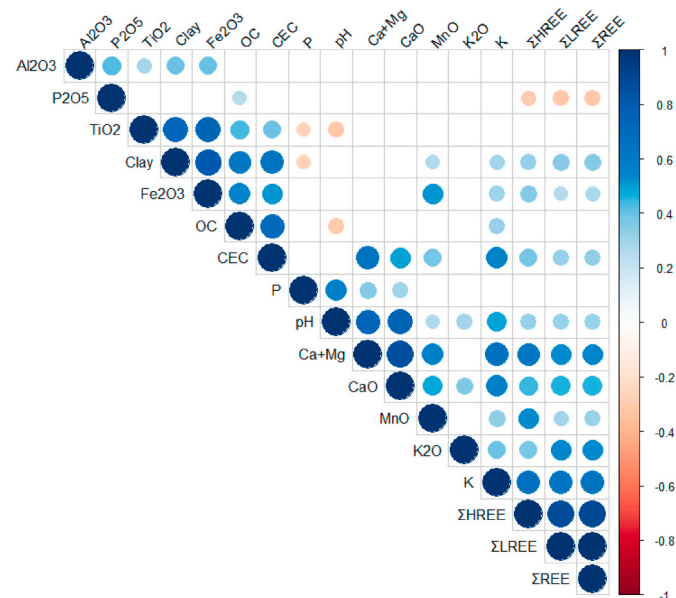

Fig. 3. Pearson's correlations matrix among REE, soil texture, and physicochemical properties ($p < 0.05$) in reference soils ($n = 61$). Positive correlations are displayed in blue and negative correlations in red color. Color intensity and the size of the circle are proportional to the correlation coefficients. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

4. Conclusions

This study provided baseline data for REE concentrations in natural and cultivated soils from different Brazilian biomes. Our findings can guide and regulate soil-REE limits considering different soil parent materials, subsidizing regulation policies in a more realistic manner for Brazilian legislators and for tropical pedoenvironments overall, being also useful for setting environmental quality standards.

The input of phosphate products - which are known for carrying REE - is likely to affect soil-REE concentrations in most geopedological contexts. This, in turn, suggests that differences in the contents of REE in agricultural soils can be attributed to land use, while those in non-agricultural soils can be credited to other factors such as parent materials, biomes, and pedogenic processes. In fact, REE-normalized patterns, REE fractionation indices, and enrichment factors allowed us to evidence that soil-REE contamination might occur via agricultural activities, such as the long-term application of products from the phosphate industry (e.g., P fertilizers and phosphogypsum) containing REE.

Finally, multiple regression models were able to accurately predict soil-REE concentrations from environmental covariates biomes, land use, and sand fraction content. Moreover, along with parent material, they also helped to predict HREE contents in particular.

Author statement

Fábio Henrique Alves Bispo: Conceptualization, methodology, investigation, visualization, formal analysis, project administration, and writing the original draft. Michele Duarte de Menezes: Investigation, formal analysis, reviewing, and editing. Ademir Fontana: Reviewing and editing. Jorge Eduardo de Souza Sarkis: Methodology, validation, and reviewing. Cristiano Moreira Gonçalves: Reviewing and editing. Teotônio Soares de Carvalho: Methodology, formal analysis, and visualization. Nilton Curi: Reviewing and editing. Luiz Roberto Guimarães Guilherme: Conceptualization, reviewing and editing, funding acquisition, supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.117972.

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