Jacques Agra Bezerra da Silva, Ygor; Williams Araújo do Nascimento, Clístenes; Jacques
Agra Bezerra da Silva, Yuri; Miranda Biondi, Caroline; Cordeiro Atanázio Cruz Silva,
Cinthia Maria
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# Rare Earth Element Concentrations in Brazilian Benchmark Soils

**Ygor Jacques Agra Bezerra da Silva**[(1)]**, Clístenes Williams Araújo do Nascimento**[(1)]**, Yuri Jacques Agra Bezerra da Silva**[(2)]**, Caroline Miranda Biondi**[(1)] **and Cinthia Maria Cordeiro Atanázio Cruz Silva**[(1)]

[(1)] Universidade Federal Rural de Pernambuco, Departamento de Agronomia, Recife, Pernambuco, Brasil.
[(2)] Universidade Federal do Piaui, Departamento de Ciência do Solo, Bom Jesus, Piaui, Brasil.

**\* Corresponding author:**
E-mail: clistenes.nascimento@
ufrpe.br

**ABSTRACT:** Studies regarding background concentrations of rare earth elements (REEs) are scarce and have mainly focused on a limited number of soil types from the northern hemisphere. The aim of this study was to determine REE concentrations in thirty-five benchmark soils of Brazil. Composite soil samples were taken from areas under native vegetation or with minimal anthropogenic influence. Concentrations of La, Ce, Pr, Nd, Sm, Eu, Gd, Yb, Lu, Dy, Er, Ho, Tb, Tm, Y, Sc, and Fe were determined by ICP-OES using a cyclonic spray chamber/nebulizer system after microwave acid digestion. Results were assessed by descriptive statistics, Pearson correlation, and principal component analysis (PCA). Regression analyses among Fe, organic carbon, and REEs were performed to provide a tool for estimating REE concentrations in soils. The REE concentrations in the Brazilian benchmark soils were in the following order: Ce > La > Nd > Pr > Y > Sm > Gd > Sc > Dy > Yb > Eu > Er > Tb > Ho > Lu > Tm. The clear decoupling between light and heavy rare earth elements in soils, indicated by multivariate analysis, is mainly related to differences in parent material. The lowest REE concentrations were found in sandy sediments, whereas the highest REE concentrations were observed in basalt, biotite gneiss, and clayey sediments. The organic carbon and Fe concentrations can properly predict REE concentrations in soils; such a finding can assist in estimating REE concentrations in soils not only in Brazil but also in similar soils developed under tropical conditions.

**Keywords:** lanthanides, scandium, yttrium, metals, trace elements.

# INTRODUCTION

Rare earth elements (REEs) are a group of metals comprised of yttrium (Y), scandium (Sc), and 14 elements of the lanthanide series (lanthanum to lutetium). These last 14 elements are generally divided into two groups: light (lanthanum to europium) and heavy (gadolinium to lutetium) elements (Hu et al., 2006; Du and Graedel, 2011; Sadeghi et al., 2013). The denomination "rare" might lead to misunderstandings since they can be as abundant in the Earth's crust as copper, nickel, or lead (Haxel et al., 2002). For instance, cerium (Ce) is the 25th most abundant element in the Earth's crust and its concentration in soil is often similar to that of Zn (Tyler, 2004). In addition, REEs are found in more than 200 minerals, mainly phosphates, carbonates, silicates, and Fe- and Mn-oxides (Henderson, 1984).

Given their unique physical and chemical properties, REEs are widely used for multiple purposes, such as industrial production of technological devices (Strauch et al., 2008; Long et al., 2010; Robert and David, 2012) and agricultural fertilizers (Pang et al., 2002; Kobayashi et al., 2007). These and other technical innovations will strongly increase REE demand in the near future; hence, accumulation of these elements in the soil may become an environmental concern (Zeng et al., 2006; D'Aquino et al., 2009; Du and Graedel, 2011).

Data on soil background concentrations of trace (Salonen and Korkka-Niemi, 2007; Biondi et al., 2011; Preston et al., 2014; Alfaro et al., 2015) and major elements (Montserrat and Camarero, 2010; Hannan and Tanguma, 2012; Dantu, 2014) are easily found in the literature. However, data regarding REEs are comparatively scarce and have mainly focused on determination of REEs in a limited number of soil types (Turra et al., 2011; Damascena et al., 2015). Given that REE concentrations are influenced by soil parent materials and pedogenesis processes, such studies are not able to estimate the variability of REE concentrations expected in soils. Thus, the study of benchmark soils can yield a set of REE data that covers a wide range of pedogeological conditions and might be used in estimation of REEs on a more national or global scale. A benchmark soil is one of large extent within one or more major land resource areas, one that holds a key position in the soil classification system, one for which there is a large amount of data, one that has special importance for one or more significant land uses, or one that is of significant ecological importance (USDA, 2004).

Geochemical associations between trace elements and Fe concentrations in soils are often reported (Hamon et al., 2004; Alfaro et al., 2015); therefore, regression equations may predict trace element concentrations in soils based on such correlations. This can avoid costly sampling and analysis when levels of potentially toxic elements need to be known for a great number of soil samples (Alfaro et al., 2015). Likewise, high correlations between Fe and REE concentrations can be useful for estimating the concentrations of REEs in soils.

Taking into account the growing global economic importance of REEs, the use of these elements in several Earth science fields (Laveuf and Cornu, 2009; Li et al., 2013; Chen et al., 2014; Abbott et al., 2015; Pagano et al., 2015), and the scarcity of data available for Brazil (Pérez et al., 1997; Paye et al., 2016) and other tropical regions, this study was carried out to determine the REE concentrations in soils of a Brazilian benchmark collection that represents all the soil orders found in the country. Additionally, we demonstrate that a geochemical association exists between Fe and REEs in these soils. Such a finding can aid in estimating and tracing REE concentrations in soils.

# MATERIALS AND METHODS

## Sampling and sample preparation

The study area extends from the coastal region to the semiarid zone of the state of Pernambuco, Brazil (Figure 1), and covers sites with different soil and geological settings.

Annual average rainfall ranges from 500 mm to 2,200 mm and air temperature ranges from 24 °C to 28 °C for semiarid and coastal regions, respectively. In the coastal zone, soils are often developed upon tertiary sediments or crystalline rocks – usually deep and highly weathered – with relief ranging from slightly to strongly rolling; vegetation is mainly composed of evergreen broad-leaf tropical forest. In the semiarid region, soils are generally shallow owing to the long dry season, which in turn decreases the chemical weathering and leaching process; vegetation is mainly deciduous forest, known locally as hypoxerophilous *caatinga*, and dense tree-shrub deciduous vegetation, classified locally as hyperxerophilous *caatinga*, somewhat similar to a dry season deciduous thornbush savannah (Nascimento et al., 2006).

A total of 35 composite topsoil samples were taken from areas covered by native vegetation or with minimal anthropogenic influence, representing a wide diversity of soil classes and parent materials (Table 1). Consequently, the soils also exhibit wide variability regarding physical and chemical properties (Table 2). Soil samples were air dried and passed through a 2-mm mesh nylon sieve, ground in an agate mortar, and passed through a stainless steel 0.3-mm mesh sieve (ABNT No. 50).

### Quality control and quality assurance (QC/QA)

For REE and Fe determination, 1.000 g of soil was digested in Teflon vessels with 9 mL of $HNO_3$ and 3 mL of HCl in a microwave oven (USEPA, 1998). This method is recommended by the Brazilian Council for the Environment to assess potentially toxic concentrations of elements in soil (Conama, 2009). All the extracts were transferred to 25 mL certified flasks (NBR ISO/IEC) filled with ultrapure water (Millipore Direct-Q System) and filtered through slow filter paper (Macherey Nagel®). High purity acids were used in the analysis (Merck PA).

Calibration curves for REE and Fe determination were prepared from standard 1,000 mg $L^{-1}$ (Titrisol®, Merck). Analysis was performed only when the coefficient of determination ($R^2$) of the calibration curve was higher than 0.999. Analytical data quality and standard operational procedures such as curve recalibration and analyses of blanks and the standard reference materials SRM 2710a Montana I Soil and SRM 2709 San Joaquin soil (NIST, 2002) were performed. All analyses were carried out in duplicate. Concentrations of La, Ce, Pr, Nd, Sm, Eu, Gd, Yb, Lu, Dy, Er, Ho, Tb, Tm, Y, Sc, and Fe were determined by inductively coupled
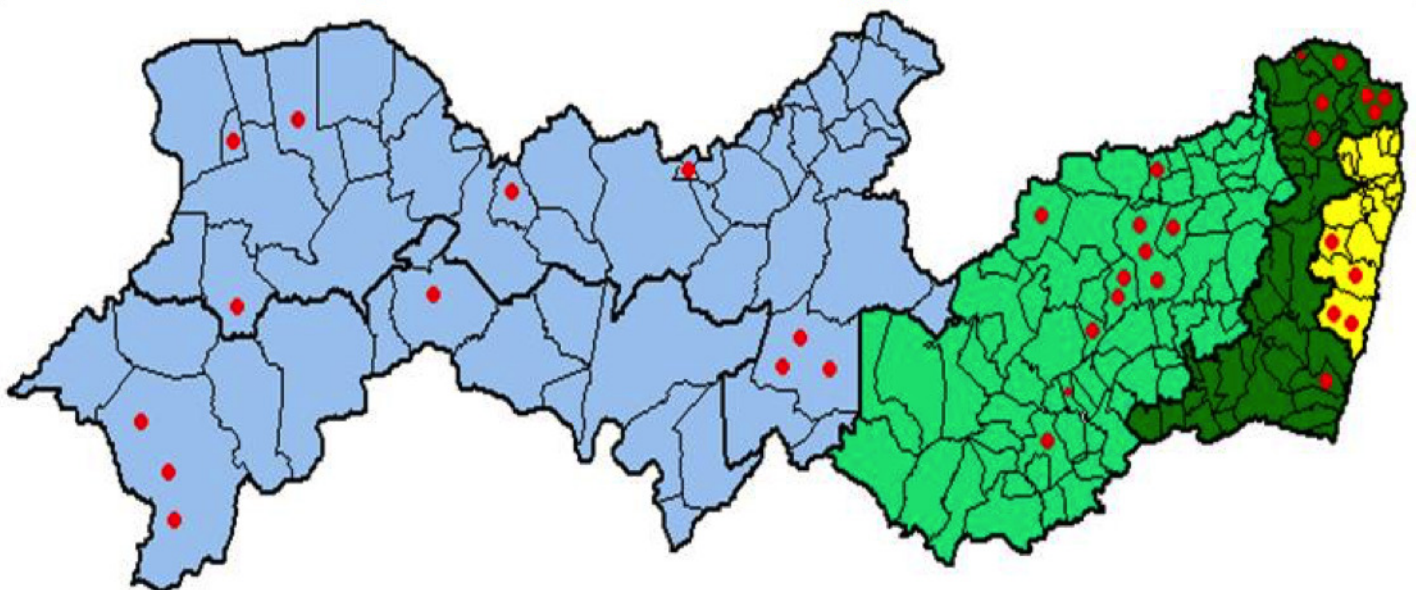


**Figure 1.** Distribution of soil sampling sites in the state of Pernambuco, Brazil.

plasma (ICP-OES/Optima 7000, Perkin Elmer); in order to improve both sensitivity and stability for REE measurements, a cyclonic spray chamber/nebulizer system was coupled to the ICP.

## Statistical analysis

Results were assessed by descriptive statistics, Pearson correlation, and principal component analysis (PCA). Principal component analysis has been widely used for studying geochemical data (Carranza, 2008; Sadeghi et al., 2013; Agnan et al., 2014; Silva et al., 2015) and consists of converting the original group of variables into a new uncorrelated group of equal dimension. Such groups are known as principal components – linear combination of the original variables – which aim to explain the maximum level of total variability associated with

**Table 1.** Soil class according to Soil Taxonomy and Brazilian System of Soil Classification, parent material, and locations of soils

| Sample | Soil class (Soil Taxonomy) | Soil class (Brazilian System of Soil Classification) | Parent material | Location |
|---|---|---|---|---|
| 1 | Ustic Kandihumult | Argissolo Vermelho-Amarelo | Gneisses | 07°25′22″S / 35°10′54″W |
| 2 | Acrudoxic Kandiudult | Argissolo Amarelo | Sandy/clayey sediments | 07°37′30″S / 34°57′30″W |
| 3 | Typic Haplorthod | Espodossolo Humilúvico | Sandy sediments | 07°38′41″S / 34°56′44″W |
| 4 | Typic Kandiudult | Argissolo Vermelho-Amarelo | Gneisses and migmatites | 08°01′42″S / 34°51′42″W |
| 5 | Udic Argiustoll | Chernossolo Argilúvico | Gneisses | 07°44′32″S / 35°14′04″W |
| 6 | Xanthic Hapludox | Latossolo Amarelo | Clayey/sandy sediments | 08°38′39″S / 35°09′15″W |
| 7 | Rhodic Kandiudult | Nitossolo Vermelho | Basalt/trachytes | 08°18′00″S / 34°59′00″W |
| 8 | Rhodic Kandiustalf | Argissolo Vermelho | Gneisses | 07°25′17″S / 35°16′23″W |
| 9 | Typic Plinthudult | Plintossolo Argilúvico | Clayey/sandy sediments | 07°37′30″S / 34°57′30″W |
| 10 | Fragic Kandiustult | Argissolo Amarelo | Sandy sediments | 07°36′20″S / 35°08′43″W |
| 11 | Fibric Tropohemist | Organossolo Háplico | Organic deposits (Holocene) | 08°27′37″S / 35°04′48″W |
| 12 | Typic Endoaquent | Gleissolo Háplico | Clayey/sandy sediments | 08°25′22″S / 35°01′14″W |
| 13 | Typic Ustortent | Neossolo Regolítico | Biotite-gneisses | 08°21′42″S / 36°10′26″W |
| 14 | Arenic Albaqualf | Planossolo Háplico | Biotite-gneisses | 08°21′28″S / 36°10′20″W |
| 15 | Typic Albaqualf | Planossolo Háplico | Diorites | 08°27′26″S / 36°12′49″W |
| 16 | Kanhaplic Haplustalf | Argissolo Vermelho | Biotite-gneisses | 08°10′21″S / 25°54′35″W |
| 17 | Typic Ustortent | Neossolo Regolítico | Biotite-gneisses | 08°13′54″S / 35°55′15″W |
| 18 | Typic Plinthustult | Argissolo Amarelo | Biotite-muscovite-quartzite | 07°52′47″S / 31°55′18″W |
| 19 | Typic Natraqualf | Planossolo Nátrico | Biotite-gneisses | 07°58′22″S / 36°11′02″W |
| 20 | Humic Hapludox | Latossolo Vermelho-Amarelo | Titanite-amphibole-biotite | 08°14′19″S / 36°10′28″W |
| 21 | Grossarenic Kandiustalf | Argissolo Vermelho-Amarelo | Biotite-muscovite-gneisses | 08°42′45″S / 36°25′00″W |
| 22 | Ustic Kandihumult | Argissolo Amarelo | Clayey sediments | 09°03′00″S / 36°29′00″W |
| 23 | Lithic Ustortent | Neossolo Litólico | Granite | 08°04′19″S / 36°03′22″W |
| 24 | Aridic Plinthustalf | Argissolo Amarelo | Sandy/clayey sediments | 09°03′46″S / 40°18′46″W |
| 25 | Aquic Natrargid | Planossolo Nátrico | Sandy sediments | 09°02′30″S / 40°15′07″W |
| 26 | Typic Quarzipsament | Neossolo Quartzarênico | Sandy sediments | 09°21′13″S / 40°28′37″W |
| 27 | Typic Aquisalid | Neossolo Flúvico | Clayey sediments | 08°43′18″S / 37°31′27″W |
| 28 | Aridic Ustifluvent | Neossolo Flúvico | Sandy sediments | 08°30′26″S / 37°37′24″W |
| 29 | Typic Quartzipsament | Neossolo Quartzarênico | Arenite | 08°38′19″S / 37°40′04″W |
| 30 | Aridic Haplustalf | Luvissolo Crômico | Gneisses/schists/phyllites | 08°30′10″S / 39°19′39″W |
| 31 | Xanthic Haplustox | Latossolo Amarelo | Sandy/clayey sediments | 07°44′33″S / 40°12′11″W |
| 32 | Oxic Ustropept | Cambissolo Háplico | Syenite | 07°48′29″S / 38°08′15″W |
| 33 | Chromic Haplustert | Vertissolo Háplico | Shale | 07°37′44″S / 40°03′14″W |
| 34 | Aridic Plinthustalf | Argissolo Amarelo | Sandy/clayey sediments | 08°19′35″S / 40°16′36″W |
| 35 | Lithic Ustortent | Neossolo Litólico | Biotite-schists | 08°00′95″S / 38°53′39″W |

these independent variables (Manly, 2008). To extract the significant principal components while diminishing the contribution of variables with little importance, we employed Varimax rotation (Kaiser, 1958). Regression analyses among Fe, organic carbon (OC), and REEs were tested to provide a tool for estimating REE concentrations in soils.

## RESULTS AND DISCUSSION

### Quality control and quality assurance (QC/QA)

Percentage recoveries of REEs from the certified materials ranged from 79 to 98 % for SRM 2710a and 52 to 93 % for SRM 2709 (Table 3). The highest recoveries were observed for Yb, Lu, Sm, and Gd: SRM 2710a (98, 97, 95, and 90 %, respectively) and SRM 2709 (93, 83, 85, and 80 %, respectively), while Nd, Ce, La, and Sc showed the lowest recoveries. Since the digestion method used (USEPA 3051A) is not able to extract REEs from silicates (NIST, 2002), in general, the lower the recovery, the higher the association of the element with these soil silicate minerals.

**Table 2.** Mean, maximum, minimum, and median concentrations and standard deviation for physical and chemical properties of Brazilian benchmark soils

| Sample | Sand | Silt | Clay | pH($H_2O$) | $Al^{3+}$ | $Ca^{2+}+Mg^{2+}$ | $K^+$ | $Na^+$ | P | OC |
|---|---|---|---|---|---|---|---|---|---|---|
| | | g kg$^{-1}$ | | | | cmol$_c$ dm$^{-3}$ | | | mg dm$^{-3}$ | g kg$^{-1}$ |
| Mean | 608.5 | 160.1 | 231.4 | 5.7 | 0.6 | 5.1 | 0.30 | 0.60 | 35.3 | 33.6 |
| Median | 640.0 | 167.0 | 180.0 | 5.5 | 0.2 | 2.7 | 0.27 | 0.09 | 7.0 | 14.0 |
| Max | 914.0 | 373.0 | 713.0 | 7.9 | 6.5 | 19.8 | 1.26 | 18.50 | 455.3 | 380.0 |
| Min | 61.0 | 18.0 | 65.0 | 4.2 | 0.0 | 0.6 | 0.08 | 0.01 | 0.0 | 5.4 |
| SD[1] | 189.7 | 86.0 | 123.6 | 0.8 | 0.7 | 4.1 | 0.20 | 1.00 | 42.4 | 29.8 |

Sand, silt, clay: pipette method (Claessen, 1997). pH in water (Claessen, 1997). $Al^{3+}$, $Ca^{2+}+Mg^{2+}$, $Na^+$: extractor KCl 1 mol L$^{-1}$ (Defelipo and Ribeiro, 1997). P, K, Na: extractor Mehlich-1 (Defelipo and Ribeiro, 1997). OC: organic carbon (Yeomans and Bremner, 1988). [1] SD: standard deviation.

**Table 3.** Mean contents of rare earth elements (REEs) recovered for certified reference material (SRM 2710a Montana soil and SRM 2709 San Joaquin soil) by USEPA method 3051A

| Metal | 2710a Montana Soil NIST | | | 2709 San Joaquin NIST | | |
|---|---|---|---|---|---|---|
| | Determined value | Certified value | Recovery | Determined value | Certified value | Recovery |
| | mg kg$^{-1}$ | | % | mg kg$^{-1}$ | | % |
| La | 12.1 | na[1] | na | 11.2 | 21.7 | 52 |
| Ce | 49.15 | 60 | 82 | 28.5 | 42 | 68 |
| Pr | 4.1 | na | na | 3.8 | na | na |
| Nd | 17.42 | 22 | 79 | 11.0 | 17 | 65 |
| Sm | 3.8 | 4.0 | 95 | 3.4 | 4.0 | 85 |
| Eu | 0.7 | 0.82 | 85 | 0.6 | 0.83 | 72 |
| Gd | 2.7 | 3.0 | 90 | 2.4 | 3.0 | 80 |
| Yb | 1.95 | 2.0 | 98 | 1.85 | 2.0 | 93 |
| Lu | 0.3 | 0.31 | 97 | 0.25 | 0.3 | 83 |
| Dy | 0.0 | na | na | 0.6 | na | na |
| Er | 0.9 | na | na | 0.8 | na | na |
| Ho | 0.1 | na | na | 0.2 | na | na |
| Tb | 0.7 | na | na | 0.65 | na | na |
| Y | 11.5 | na | na | 11.0 | na | na |
| Sc | 8.1 | 9.9 | 82 | 7.6 | 11.1 | 68 |

[1] na: not available.

## REEs concentration in soils

Average REE concentrations in soils were in the following order: Ce > La > Nd > Pr > Y > Sm > Gd > Sc > Dy > Yb > Eu > Er > Tb > Ho > Lu > Tm (Figure 2). The REE concentrations in the soil is mainly governed by parent materials (Liu, 1988; Hu et al., 2006), but weathering conditions, organic matter, and clay concentrations are also important to determine these levels (Tyler, 2004). The abundance of REEs found here is very similar to that reported for soils of Brazil (Paye et al., 2016) and other countries (Wei et al., 1991; Yoshida et al., 1998; Tyler and Olsson, 2002; Sadeghi et al., 2013) and follows the Oddo-Harkins rule, which holds that elements with an even atomic number (such as Ce) are more common than elements with an odd atomic number (such as La).

The average Ce and La concentrations (43.48 and 20.79 mg kg$^{-1}$, respectively) were higher than those for Zn and Cu (19.61 and 9.25 mg kg$^{-1}$); Pr and Nd (9.61 and 17.70 mg kg$^{-1}$) were also found in higher concentrations than trace elements (Ni and Co) measured in the same soils (Biondi et al., 2011). In addition, the average Gd concentration was greater than the average Cd concentration generally found in Brazilian soils (Paye et al., 2010; Santos and Alleoni, 2013; Preston et al., 2014). Tm, Lu, Ho, and Tb were the least abundant heavy rare earth elements (HREEs) in soils; their values are comparable to those often reported for Mo and are related to the very low concentration in primary minerals.

The lowest sum of REEs occurred in soils derived from sandy sediments: profiles 28 (9.26 mg kg$^{-1}$), 25 (9.54 mg kg$^{-1}$), 3 (13.31 mg kg$^{-1}$), and 10 (14.84 mg kg$^{-1}$) (Table 1). Studying REE distribution in Sweden, Sadeghi et al. (2013) also observed the lowest contents in sandstones. The highest REE concentrations in Brazilian benchmark soils were derived from basalt, biotite gneiss, and clayey sediments, profiles 7 (549 mg kg$^{-1}$), 16 (525 mg kg$^{-1}$), and 12 (410 mg kg$^{-1}$), respectively. The sum of light rare earth elements (LREEs) in soils was equal to 95.56 mg kg$^{-1}$.  The maximum LREE concentrations were observed for the soil with the highest clay content (Figure 2). These values are much higher than the average in the Earth's crust and indicate that LREE enrichment took place in these soils. Several authors report LREE accumulation in clayey soils (Minarik et al., 1998; Dong et al., 2001; Kanazawa and Kamitani, 2006; Prudêncio et al., 2011; Ahn et al., 2014).

The sum of REEs in soils of Brazil was 107.54 mg kg$^{-1}$; this value is slightly higher than the average concentrations in Japan and Sweden, but lower than those in China and Europe
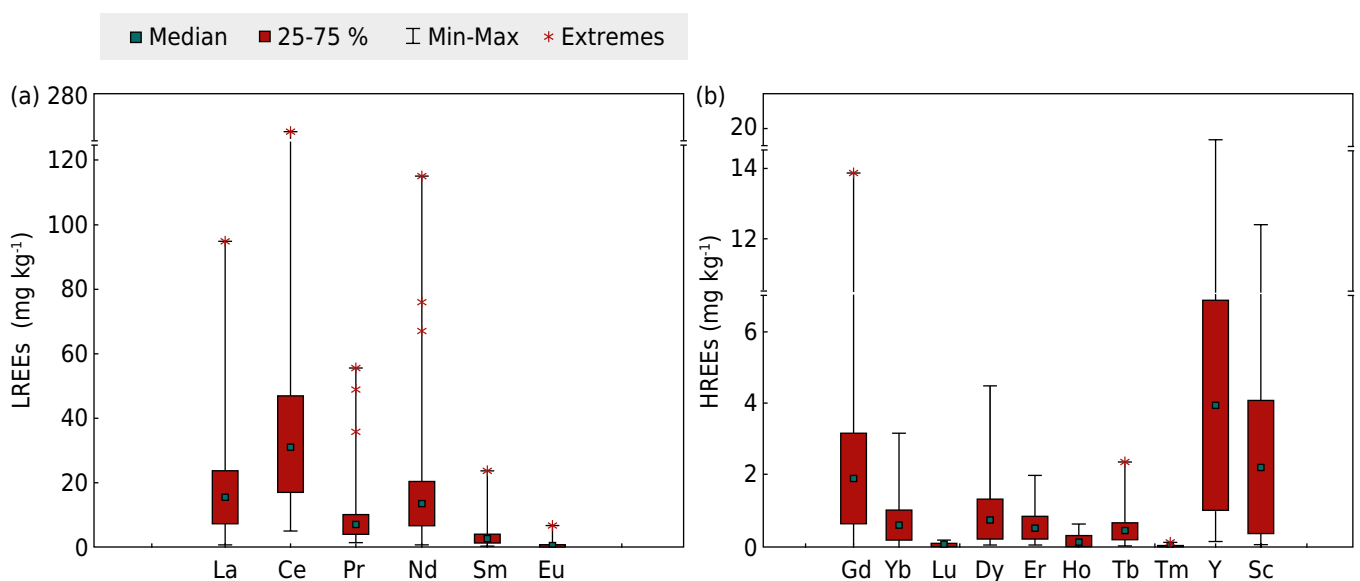


**Figure 2.** Data on the concentrations of light rare earth elements (LREE) (a) and heavy rare earth elements (HREE) (b) in Brazilian benchmark soils.

(Table 4). The higher REE concentration in China is due to rich soil parent materials that comprise 23 % of the world's proven reserves (18.59 Mt, in 2009) (TSCIOPRC, 2012).

## Correlation matrix

Significant positive correlations among REEs were observed (Table 5). The correlation coefficients ranged from 0.54 (Ce-Er) to 0.99 (Ce-Pr), at $p<0.05$ and $p<0.01$, respectively. The highest correlations were observed among the following LREEs: La-Ce (0.96), La-Pr (0.97), Ce-Pr (0.99), and Pr-Nd (0.96), and the HREEs: Gd-Y (0.94), Dy-Ho (0.94), Dy-Tb (0.95), and Er-Ho (0.96). High correlations among REEs serve as useful tracers in the environment. Organic C and Fe contents play an important role in LREE and HREE distribution, respectively; however, a clear relationship between clay content and LREEs and HREEs was not observed in the matrix correlation; therefore, multivariate statistical analysis was used to further address this relationship.

## Principal component analysis

Principal component analysis (PCA) was carried out based on the strong positive correlation among REEs and their multivariate normal distribution. The entire data set showed principal components (PC) with eigenvalues higher than unity and explained roughly 89 % of the total variance of REE distribution. PC1 and PC2 accounted for 80 and 8.9 % of total variance, respectively (Figure 3). PC1 had the highest loadings for Eu (0.66), Gd (0.80), Yb (0.83), Lu (0.84), Dy (0.77), Er (0.92), Ho (0.83), Tb (0.74), Y (0.83), Sc (0.80), Fe (0.76), and Clay (0.61), whereas PC2 was mainly correlated with La (0.90), Ce (0.94), Pr (0.94), Nd (0.86), Sm (0.77), and organic carbon (OC) (0.90). The clear decoupling between LREEs (PC2) and HREEs (PC1 – except for Eu) in soils is mainly related to differences in parent material, atomic weight, ionic radii, coordination numbers (c.n.), and electronegativity (Henderson, 1984; Laveuf and Cornu, 2009). For instance, LREEs often occupy the larger sites of 8-10 c.n. and concentrate in carbonates and phosphates, whereas HREEs usually occupy 6-8 c.n. sites

**Table 4.** Mean concentrations of rare earth elements (REEs) in soils of Brazil compared to international soil data and Earth's crust

| Element | Brazil | Japan | China | Sweden | European average | Earth's crust |
|---|---|---|---|---|---|---|
| | | | mg kg$^{-1}$ | | | |
| La | 20.79 | 18.00 | 37.4 | 17.42 | 25.90 | 35.00 |
| Ce | 43.48 | 40.00 | 64.7 | 37.67 | 52.2 | 66.00 |
| Pr | 9.61 | 4.50 | 6.67 | 4.10 | 6.02 | 9.10 |
| Nd | 17.70 | 18.00 | 25.1 | 15.14 | 22.40 | 40.00 |
| Sm | 3.37 | 3.70 | 4.94 | 2.98 | 4.28 | 7.00 |
| Eu | 0.6 | 1.0 | 0.98 | 0.65 | 0.85 | 2.1 |
| Gd | 2.32 | 3.70 | 4.38 | 3.07 | 4.20 | 6.10 |
| Yb | 0.67 | 2.00 | 2.32 | 2.01 | 2.09 | 3.10 |
| Lu | 0.05 | 0.3 | 0.35 | 0.30 | 0.30 | 0.80 |
| Dy | 0.93 | 3.3 | 3.93 | 2.95 | 3.58 | 4.5 |
| Er | 0.59 | 2.0 | 2.42 | 1.88 | 2.1 | 3.5 |
| Ho | 0.17 | 0.7 | 0.83 | 0.61 | 0.72 | 1.3 |
| Tb | 0.5 | 1.2 | 0.58 | 0.49 | 0.64 | 1.2 |
| Y | 4.45 | na[1] | na | na | na | 31.00 |
| Sc | 2.31 | na | na | na | na | na |
| ∑LREE | 95.56 | 85.2 | 139.79 | 77.96 | 111.65 | 159.2 |
| ∑HREE | 11.99 | 13.2 | 14.81 | 11.31 | 13.63 | 51.5 |
| ∑REE | 107.54 | 98.4 | 154.6 | 89.27 | 125.28 | 210.7 |
| Reference | This study | Yoshida et al. (1998) | Wei et al. (1991) | Sadeghi et al. (2013) | Sadeghi et al. (2013) | Tyler and Olsson (2002) |

[1] na: not available.

**Table 5.** Pearson correlation matrix between rare earth elements (REEs), Fe, clay and organic carbon (OC)

| | La | Ce | Pr | Nd | Sm | Eu | Gd | Yb | Lu | Dy | Er | Ho | Tb | Y | Sc | Fe | Clay | OC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| La | 1.00 | | | | | | | | | | | | | | | | | |
| Ce | **0.96** | 1.00 | | | | | | | | | | | | | | | | |
| Pr | **0.97** | **0.99** | 1.00 | | | | | | | | | | | | | | | |
| Nd | **0.95** | **0.93** | **0.96** | 1.00 | | | | | | | | | | | | | | |
| Sm | **0.90** | **0.86** | **0.89** | **0.98** | 1.00 | | | | | | | | | | | | | |
| Eu | **0.71** | **0.64** | **0.70** | **0.87** | **0.94** | 1.00 | | | | | | | | | | | | |
| Gd | **0.78** | **0.71** | **0.73** | **0.87** | **0.91** | **0.87** | 1.00 | | | | | | | | | | | |
| Yb | **0.75** | **0.66** | **0.69** | **0.83** | **0.87** | **0.85** | **0.91** | 1.00 | | | | | | | | | | |
| Lu | **0.61** | <u>0.55</u> | <u>0.56</u> | **0.64** | **0.66** | <u>0.57</u> | **0.82** | **0.79** | 1.00 | | | | | | | | | |
| Dy | **0.78** | **0.73** | **0.77** | **0.88** | **0.91** | **0.85** | **0.92** | **0.86** | **0.80** | 1.00 | | | | | | | | |
| Er | **0.60** | <u>0.54</u> | <u>0.56</u> | **0.69** | **0.73** | **0.69** | **0.88** | **0.88** | **0.93** | **0.90** | 1.00 | | | | | | | |
| Ho | **0.66** | **0.62** | **0.63** | **0.73** | **0.76** | **0.67** | **0.87** | **0.80** | **0.90** | **0.94** | **0.96** | 1.00 | | | | | | |
| Tb | **0.82** | **0.80** | **0.82** | **0.92** | **0.94** | **0.87** | **0.93** | **0.91** | **0.81** | **0.95** | **0.88** | **0.88** | 1.00 | | | | | |
| Y | **0.77** | **0.67** | **0.69** | **0.82** | **0.85** | **0.78** | **0.94** | **0.91** | **0.86** | **0.93** | **0.92** | **0.92** | **0.88** | 1.00 | | | | |
| Sc | **0.69** | <u>0.59</u> | **0.62** | **0.78** | **0.85** | **0.87** | **0.86** | **0.94** | **0.71** | **0.82** | **0.80** | **0.74** | **0.85** | **0.87** | 1.00 | | | |
| Fe | **0.60** | <u>0.54</u> | <u>0.58</u> | **0.73** | **0.80** | **0.85** | **0.81** | **0.91** | **0.67** | **0.73** | **0.76** | **0.64** | **0.86** | **0.71** | **0.85** | 1.00 | | |
| Clay | **0.70** | <u>0.56</u> | <u>0.58</u> | **0.69** | **0.72** | **0.68** | **0.70** | **0.82** | <u>0.58</u> | **0.64** | **0.63** | <u>0.55</u> | **0.69** | **0.73** | **0.80** | **0.75** | 1.00 | |
| OC | **0.98** | **0.98** | **0.99** | **0.98** | **0.93** | **0.76** | **0.81** | **0.77** | **0.63** | **0.83** | **0.64** | **0.70** | **0.87** | **0.78** | **0.71** | **0.65** | **0.66** | 1.00 |

Bold: significant at $p < 0.01$; underlined: significant at $p < 0.05$.

and are predominant in oxides and some phosphates (Kanazawa and Kamitani, 2006). REE distribution and mineralization data in Sweden also exhibited two distinct groupings – HREEs and LREEs in soils (Sadeghi et al. (2013). Based on their results, the major difference was related to the distribution patterns in the parent material underlying northern Sweden.

The highest loadings for OC with LREES and Fe with HREEs (Figure 3) clearly suggest their geochemical association. Organic C seems to have little influence on HREE distribution; furthermore, as incorporation of REEs in the Fe-Mn-oxide structure is limited, REEs rarely substitute Fe in the of Fe-oxide lattice (Braun et al., 1993). Such assumptions give rise to the question: Could Fe and/or OC be good predictors of REE concentrations in soils? As a matter of fact, we found a well-defined natural association between Fe and the sum of HREEs (Figure 4b), as well as between OC and the sum of LREEs (Figure 4a).

Linear regression analyses were carried out to address the geochemical association between individual REEs and Fe and OC concentrations. Coefficients of determination ranged from 0.40 to 0.97 (Table 6). As suggested by PCA, HREEs were strongly associated with Fe concentration in soils, whereas LREEs were poorly associated with Fe contents, except for Nd, Sm, and Eu, which were regarded as medium REEs (Laveuf and Cornu, 2009). Moreover, the highest standard error of estimate values observed, the measure of the accuracy of predictions for a regression line, was for La (20), Ce (47), Pr (10), and Nd (16).

Iron accounted for 82 and 74 % of the variation of Yb and Tb distribution (Table 6). Significant correlations demonstrated that Fe is useful in predicting HREE (including medium REEs, such as Sm and Eu) background concentrations in benchmark soils not only in Brazil but concentrations under tropical soil conditions when equations are properly calibrated on a more global scale. Nevertheless, attempts must be made in order to not extrapolate Fe concentrations ranging from 840 to 94,500 mg kg$^{-1}$, respectively. The high geochemical association between Fe and HREEs might be related to preferential scavenging of the HREEs by pedogenic minerals, most probably Fe-oxyhydroxides (Brioschi et al., 2013). The influence of Fe oxide contents on the bioavailability of REEs was also reported by Fang et al. (2007). The ongoing release of HREEs during the dissolution

of Fe oxyhydroxides suggested that these elements are preferentially associated with Fe oxyhydroxides (Pédrot et al., 2015). Significant positive correlations (p<0.01) between Fe oxides and REEs (except for Ce) were obtained in agricultural soils from German (Loell et al., 2011); however, no significant correlation was observed between OC and REEs (except for Ce). They suggested that Fe oxides seem to trap Ce based on positive Ce anomaly in crystalline oxides or concretions; in addition, the complexation capacity of organic C is higher with Ce than with other REEs.
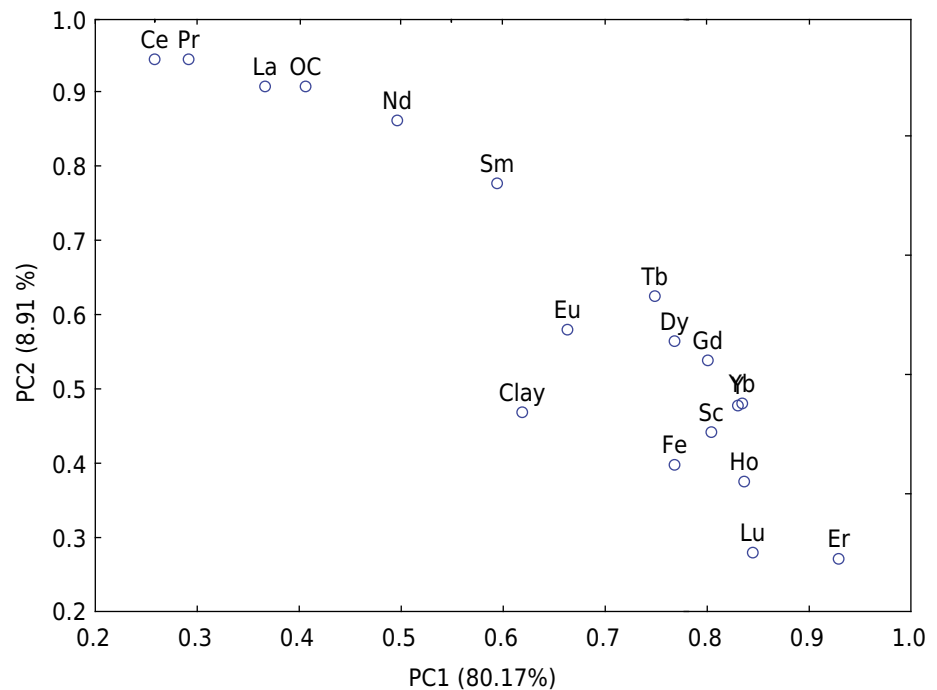


**Figure 3.** Principal component analysis of rare earth elements (REEs) in Brazilian soils.



LREEs = -3.6491 + 0.9225*OC; r² = 0.99; p < 0.0001

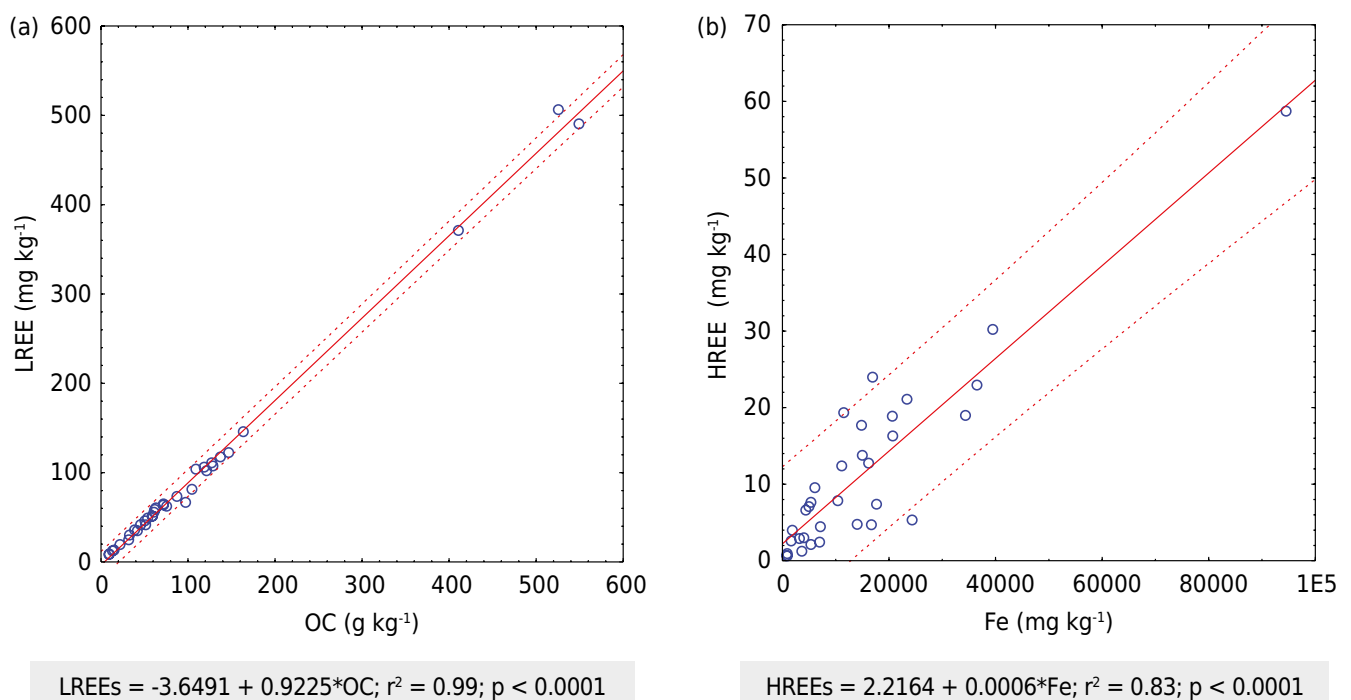HREEs = 2.2164 + 0.0006*Fe; r² = 0.83; p < 0.0001

**Figure 4.** Relationship between light rare earth elements (LREE) and organic carbon (OC) (a) and heavy rare earth elements (HREE) and Fe (b) concentrations.

**Table 6.** Regression parameters for the association between rare earth elements (REEs) and concentrations of organic carbon (OC) and Fe in soils

| Element | Slope coefficient | Constant | SEE | r | $r^2$ | p |
|---|---|---|---|---|---|---|
| | | | OC | | | |
| La | 0.19 | 0.47 | 4.31 | 0.98 | 0.97 | 0.0001 |
| Ce | 0.42 | -2.08 | 10.87 | 0.98 | 0.96 | 0.0001 |
| Pr | 0.09 | -0.45 | 1.85 | 0.98 | 0.97 | 0.0001 |
| Nd | 0.17 | -1.43 | 4.57 | 0.98 | 0.96 | 0.0001 |
| Sm | 0.03 | -0.02 | 1.57 | 0.93 | 0.87 | 0.0001 |
| | | | Fe | | | |
| Eu | 0.000054 | -0.28 | 0.61 | 0.85 | 0.72 | 0.0001 |
| Gd | 0.0001 | 0.26 | 1.69 | 0.80 | 0.65 | 0.0001 |
| Yb | 0.000032 | 0.14 | 0.27 | 0.90 | 0.82 | 0.0001 |
| Lu | 0.0000019 | 0.016 | 0.039 | 0.67 | 0.44 | 0.0001 |
| Dy | 0.000037 | 0.32 | 0.63 | 0.73 | 0.53 | 0.0001 |
| Er | 0.00002 | 0.25 | 0.32 | 0.75 | 0.57 | 0.0001 |
| Ho | 0.0000057 | 0.08 | 0.12 | 0.63 | 0.40 | 0.0001 |
| Tb | 0.000021 | 0.14 | 0.23 | 0.86 | 0.74 | 0.0001 |
| Y | 0.0002 | 1.38 | 3.42 | 0.71 | 0.50 | 0.0001 |
| Sc | 0.0001 | 0.40 | 1.35 | 0.84 | 0.71 | 0.0001 |

SEE: standard error of estimate; r: correlation coefficient; $r^2$: regression coefficient.

## CONCLUSIONS

Average REE concentrations in benchmark soils of Brazil were in the following order: Ce > La > Nd > Pr > Y > Sm > Gd > Sc > Dy > Yb > Eu > Er > Tb > Ho > Lu > Tm and were related to underlying parent material. The lowest REE concentrations were found in sandy sediments, whereas the highest REE concentrations were observed in basalt, biotite gneiss, and clayey sediments.

Organic carbon and Fe concentrations can properly predict REE concentrations in the soils studied; this finding can assist in estimating REE concentrations in soils not only in Brazil but in similar soils developed under tropical conditions.

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