MATHEUS DA SILVA FERREIRA

NATURAL BACKGROUND VALUES, GEOCHEMICAL MOBILITY AND BIOACCESSIBILITY OF RARE EARTH ELEMENTS IN SOILS OF BRAZILIAN AMAZON

Thesis presented to the Universidade Federal de Viçosa, as part of the requirements of the Graduate Program in Soil and Plants Nutrition, to obtain the title of *Doctor Scientiae*.

Advisor: Mauricio Paulo Ferreira Fontes

Co-advisor: Hedinaldo Narciso Lima

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“Forget your lust for the rich man's gold
All that you need is in your soul
And you can do this, if you try
Be a simple man”

(Simple Man - Lynyrd Skynyrd song, 1973)

ABSTRACT

FERREIRA, Matheus da Silva, D.Sc., Universidade Federal de Viçosa, July 2021. **Natural background values, geochemical mobility and bioaccessibility of rare earth elements in soils of Brazilian Amazon.** Adviser: Maurício Paulo Ferreira Fontes. Co-adviser: Hedinaldo Narciso Lima.

Rare earth elements (REEs) have been the subject of several researches in recent years, due to their use in high-tech industries or to potential toxicity. Normally, the levels of REEs in the soil are low and do not cause effects to human health, however the anthropic action can increase the levels of these elements and consequently increase the risks associated with the REEs exposure. Thus, studies about the levels of REEs in pristine and urban soils and REEs availability for living organisms are necessary. The main of this thesis were to determine the quality reference values of soil (QRV) based on natural levels, performed the geochemical fractionation and bioavailability of La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy , Ho, Er, Tm, Yb, Lu, Y and Sc in soils of the Brazilian Amazon. The soil samples used were obtained both in pristine environments (without anthropic action) and in urban environments, the samples were collected in the 0-20 cm and 60-80 cm layers. The soils of the Brazilian Amazon present variations of REE concentrations because of the dynamic interaction between geological characteristics, sediment deposits and anthropic inputs. However, the ecological risk associated with the contamination of REEs was considered low in urban soils. The QRVs recommendations for soils of the Brazilian Amazon should be based on the 90th percentile of the contents obtained from the soils sample population. The geochemical fractionation exhibited that the most bioavailable fractions of the soil (exchangeable phase, organic matter phase and Fe / Mn oxides phase) presented low levels and represented less than 20% of the total levels of REEs in all sampled soils. Oral bioaccessibility contents obtained by two *in vitro* methods (gastric protocol and gastric-intestinal protocol) and by single extractions represented less than 20% of the total content of the REEs. Non-carcinogenic risks and carcinogenic risks associated with oral exposure to REE were considerably low both for children and for adults in all soil samples from the Amazon.

Keywords: Natural contents. Enrichment. Toxic Elements. Health Risk

RESUMO

FERREIRA, Matheus da Silva, D.Sc., Universidade Federal de Viçosa, julho de 2021. **Valores naturais, mobilidade geoquímica e bioacessibilidade de elementos terras raras em solos da Amazônia brasileira.** Orientador: Maurício Paulo Ferreira Fontes. Coorientador: Hedinaldo Narciso Lima.

Os elementos terras raras (ETRs) tem sido objeto de várias pesquisas nos últimos anos, seja por sua utilização em produtos de alta tecnologia ou por sua importância ambiental. Normalmente, os teores de ETRs no solo são baixos e não acarretam problemas a saúde humana, contudo a ação antrópica pode causar o aumento dos teores desses elementos e consequentemente aumentam os riscos associados a exposição desses elementos. Assim, trabalhos que investiguem a distribuição dos teores de ETRs (naturais ou enriquecidos) e sua disponibilidade para os organismos vivos fazem-se necessários. Diante deste cenário, objetivou-se determinar os valores de referência de qualidade do solo (VRQ) baseado nos teores naturais, a mobilidade geoquímica e a biodisponibilidade de La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y e Sc em solos da Amazônia brasileira. As amostras de solo utilizadas foram obtidas tanto ambientes naturais (sem ação antrópica) quanto em ambientes urbanos, sendo amostradas nas camadas de 0-20 cm e 60-80 cm. Os solos estudados apresentaramm grandes variações de concentrações de ETRs como resultado da interação entre características geológicas, depósitos de sedimentos e influencias antrópicas. No entanto, o risco ecológico associado à contaminação de REEs foi considerado baixo em solos urbanos. As recomendações VRQs para os solos da Amazônia brasileira devem ser baseadas no percentil 90 dos teores obtidos da população amostral. A mobilidade geoquímica mostrou que as frações mais biodisponíveis do solo (fase trocável, fase matéria orgânica e fase óxidos Fe / Mn) apresentaram baixos teores e representaram menos de 20% dos teores totais de ETRs em todos os solos amostrados. A bioacessibilidade oral obtida por dois métodos *in vitro* (protocolo gástrico e protocolo gástrico-intestinal) e por extrações simples apresentou teores que representam menos de 20% do conteúdo total do ETRs. Os riscos não carcinogênicos e os riscos carcinogênicos associados à exposição oral aos ETRs foram consideravelmente baixos para crianças e adultos em todas as amostras de solo da Amazônia.

Palavras-chave: Teores Naturais. Enriquecimento. Elementos Tóxicos. Risco a Saúde

SUMMARY

GENERAL INTRODUCTION

The term Rare Earth Elements (REEs) groups 17 elements (lanthanides, Sc and Y), which have similar physicochemical proprieties and occur in the same ores (Aide e Aide, 2012). REEs are divided in light (La to Sm) and heavy (Eu to Lu, Sc and Y). The light REEs (LREE) are characterized by its small atomic mass, high solubility and alkalinity. While, the heavy REEs (HREE) are characterized by lower solubility and lower atomic mass when compared to the LREE (Ramos et al., 2016). The REEs normally present 3+-oxidation state and an electronegativity close to elements such as Ca and Na. Thus, the REEs preferentially form ionic than covalent bindings (Aide e Aide, 2012; Ramos et al., 2016).

The occurrence of REEs in soils can be very common due to the huge diversity of minerals containing these elements, such as phosphates, carbonates, silicates and oxides (Loell et al., 2011; Ramos et al., 2016). Normally, the REEs concentration in soils do not represent an environmental risk but recent studies have reported that REEs concentration may be enriched by anthropic activities such as mining, fertilizers, and industrial activity (Pagano et al., 2015a).

The REEs geochemistry pattern and their possible impacts on ecosystem have been investigated of several researchers involving soils of different parts of the world (Ramos et al., 2016). However, data about REEs in tropical soils are scarce and normally are restricted to determine the total concentration of these elements, which make the geochemical pattern and the potential of contamination of REE are relatively unknown.

Thus, this study present the first REE assessment in soils of the two biggest hydrographic basins (Solimões and Rio Negro) of the Brazilian Amazon biome and generate data to establish their Quality Reference Values (QRV) for REEs pollution. Additionally, it was performed the geochemical characterization, determination of the bioaccessible concentration and the health human risk associated to exposure of REEs in representative Amazon topsoils. It was also tested the hypothesis that REE bioaccessible fraction in those topsoils and their health human risk may be measured by a single extraction using an unbuffered mild extractor (0.01 mol L^{-1} $CaCl_2$) or a diluted acid extractors (0.43 mol L^{-1} HNO_3).

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CHAPTER 1: GEOCHEMICAL SIGNATURES AND NATURAL BACKGROUND VALUES OF RARE EARTH ELEMENTS IN SOILS OF BRAZILIAN AMAZON

ABSTRACT

FERREIRA, Matheus da Silva, D.Sc., Federal University of Viçosa, July, 2021. **Geochemical signatures and natural background values of rare earth elements in soils of Brazilian amazon.** Adviser: Maurício Paulo Ferreira Fontes. Co-adviser: Hedinaldo Narciso Lima.

Rare earth elements (REEs) are generally defined as a homogenous group of elements with similar physical-chemical properties, encompassing Y and Sc and the lanthanides elements series. Natural REEs concentration in soils depend on the parent material, the soil genesis processes and may be gradually added to the soil by anthropogenic activities. The REEs have been considered emerging pollutants in several countries, so the establishment of regulatory guidelines is necessary to avoid environmental contamination. In Brazil, REE soils data are restricted to some regions, and knowledge about them in the Amazon soils is scarce, although this biome covers more than 50% of the Brazilian territory. Thus, the objectives of this study were to determine the REE concentration in soils of two hydrographic basins (Solimões and Rio Negro) of the Amazon biome, establish their Quality Reference Values (QRV) and to investigate the existence of enrichment of REEs in urban soils. The **Σ**REE(Y+Sc) concentration of Solimões surface samples was 109.28 mg kg^{-1} and the **Σ**REE(Y+Sc) concentration in the subsurface samples was 94.11 mg kg^{-1}. In soils of Rio Negro basin, the **Σ**REE(Y+Sc) was 43.95 mg kg^{-1} surface samples and 38.40 mg kg^{-1} in subsurface samples. The **Σ**REE(Y+Sc) in urban topsoils samples was 38.62 mg kg^{-1}. The REEs concentration pattern in three studied areas are influenced in different amplitude by natural soil properties. The REEs concentration in urban topsoils were slightly higher than the Rio Negro pristine soils, but the ecological risk was low. QRVs recommend for Solimões soils ranged from 0.01 (Lu) to 145.6 mg kg^{-1} (Ce) and for Rio Negro soils ranged from 0.05 (Lu) to 15.8 mg kg^{-1} (Ce).

Keywords: Emergent contaminants. Urban Ecosystem. Lanthanides. Yttrium. Solimões. Rio Negro

RESUMO

FERREIRA, Matheus da Silva, D.Sc., Universidade Federal de Viçosa, Julho, 2021. **Assinaturas geoquímica e valores naturais de elementos de terras raras em solos da Amazônia brasileira.** Orientador: Maurício Paulo Ferreira Fontes. Coorientador: Hedinaldo Narciso Lima.

Elementos de terras raras (REEs) são geralmente definidos como um grupo homogêneo de elementos com propriedades físico-químicas semelhantes, englobando Y e Sc e a série de elementos dos lantanídeos. Os teores naturais de REEs em solos dependem do material original, dos processos de gênese do solo e podem ser gradualmente adicionados ao solo por atividades antrópicas. Os REEs têm sido considerados poluentes emergentes em diversos países, portanto o estabelecimento de diretrizes regulatórias é necessário para evitar a contaminação ambiental. No Brasil, os dados de REE no solo são restritos a algumas regiões, e o conhecimento sobre eles nos solos da Amazônia é escasso, embora este bioma cubra mais de 50% do território brasileiro. Assim, os objetivos deste estudo foram determinar a concentração de REEs em solos de duas bacias hidrográficas (Solimões e Rio Negro) do bioma Amazônico, estabelecer seus Valores de Referência de Qualidade (QRV) e investigar a existência de enriquecimento de REE em solos urbanos. O valor de **Σ**REE (Y + Sc) das amostras de superfície do Solimões foi de 109,28 mg kg^{-1} e o valor de **Σ**REE (Y + Sc) das amostras de subsuperfície foi de 94,11 mg kg^{-1}. Em solos da bacia do Rio Negro, o **Σ**REE (Y + Sc) foi de 43,95 mg kg^{-1} em amostras de superfície e 38,40 mg kg^{-1} em subsuperfície. O **Σ**REE (Y + Sc) em amostras superficiais de solo urbano foi de 38,62 mg kg^{-1}. O padrão de REEs nas três áreas estudadas é influenciado em diferentes amplitudes pelas propriedades naturais do solo. O conteúdo de REEs em solos urbanos foi ligeiramente mais alto do que nos solos naturais do Rio Negro, mas o risco ecológico foi baixo. Os QRVs recomendados para solos do Solimões variaram de 0,01 (Lu) a 145,6 mg kg^{-1} (Ce) e para os solos do Rio Negro variaram de 0,05 (Lu) a 15,8 mg kg^{-1} (Ce).

Palavras-chave: Contaminantes emergentes. Ecossistema Urbano. Lantanídeos. Ítrio. Solimões. Rio Negro

INTRODUCTION

Rare earth elements (REEs) are generally defined as a homogenous group of elements, which encompasses Y (Yttrium) and Sc (Scandium) and the elements of the lanthanides series (Hu et al., 2006; Laveuf et al., 2008). The REEs have similar chemical properties and normally tend to occur in the same ore deposits (Hu et al., 2006; Aide e Aide, 2012). Frequently, the REEs are grouped based on their atomic numbers and mass in two groups: the light REEs (La to Eu) and heavy REEs (Gd to Lu) (Laveuf e Cornu, 2009). Despite the term "rare", the occurrence of REEs in soils is very common due to the huge diversity of minerals containing these elements, such as metal phosphates, carbonates, silicates and oxides (Ramos et al., 2016). However, Promethium (Pm) undergoes fast radioactive decay (half-life is 2.62 years), which means the Pm presence in the natural condition is virtually nonexistent in the earth's crust (Migaszewski e Gałuszka, 2015; Khan et al., 2017a).

In recent decades, the interest about REEs have been increasing due to the use of REEs in industrial production of high technological devices, agricultural fertilizers and animals feed additive (Laveuf e Cornu, 2009; Schwabe et al., 2012). The use of REEs in various industrial products has resulted in increased demand for these elements in many countries (Ramos et al., 2016). The global demand for these elements was around 30 thousand tons for the years 2014 to 2020 (Tyler, 2004; Weng et al., 2015).

REE data for tropical soils are scarce and limited to a few different soils, which results in a limited knowledge about REEs geochemistry in tropical environments. In addition, data of REEs in Brazilian soil are restricted to soils from the southeast, south, and northeast regions (Boulangé e Colin, 1994; Graf et al., 1994; Sá Paye et al., 2016; Silva et al., 2016; Pereira et al., 2019). In the northern region, studies about REEs geochemistry are incipient, especially in the Amazon biome which represents about 50% of the Brazilian territory (Costi et al., 2009; Cunha et al., 2012).

The Amazon biome is rich in species diversity, being the largest tropical rainforest of the world, containing thousands of animal and plant species (Zemp et al., 2017). The Amazon is the world's largest river drainage system representing 20% of the fresh water of the world. The Amazon region has diverse geological settings formed in different geologic events, such as the uplift of the Andes. Since then, the Andes sediments have been enriching the Solimões waters, which influences the regional elemental distributions (Horbe et al., 2004; Horbe e Costa, 2005; Guimarães et al., 2013; Mendonça et al., 2015; Rousseau et al., 2019). Furthermore, in the Amazon, trace elements have been enriched in soil, water, sediments and plants due to anthropic activities (Moreira et al., 2018; Oliveira et al., 2018; Ferreira et al., 2020).

The literature have reported that the concentration of REEs in soils are influenced by the parent material, pedogenic processes, and soil characteristics like texture, organic matter and clay mineralogy (Laveuf et al., 2008; Laveuf e Cornu, 2009). Several studies have shown that REEs can be easily enriched by anthropic activities such as mining, fertilizers, and industrial activity (Zhang et al., 2001; Wu et al., 2017). The socioenvironmental impacts caused by the anthropic increase of REEs in the soil has received great attention in recent years by researchers. Studies have shown that the accumulation of REEs in the human body can cause chronic liver and kidney problems, promoting blood vessel calcification, neurological problems and pneumoconiosis (Zhu et al., 1997; Zhang et al., 2000; Meryem et al., 2016). The REEs may also enter into cell organelles and make chemical bonding with biological macromolecules, which may damage cellular structure in the human body leading to decrease in the levels of total serum protein, albumin, globulin, serum triglycerides, immunoglobulin and raise cholesterol levels in the blood (Wei et al., 2013; Gonzalez et al., 2014).

Normally, REE assessment in soil, and the potential environmental risk, are obtained using methods developed for trace elements such as Cd, Pb and Cr (Hakanson, 1980; Chen et al., 2020). Indexes such as Enrichment Factor (EF) and Geoaccumulation Index (Igeo) are used in studies to evaluate the enrichment of REEs in soils (Franklin et al., 2016; Tripathee et al., 2016). The potential Ecological Risks Index (PERI), introduced by Hakanson (1980), is a widely used to evaluate the degree of trace elements pollution (Islam et al., 2015). Recently, this index was used to evaluate the potential risk of REEs in soils from the Tibet Plateau (Wu et al., 2019), and the toxicity coefficients of 15 REEs were established based in average concentration of China soils and World soil (Chen et al., 2020). This index is becoming an important option to estimate the contamination risks in ecosystems induced by high levels of REEs in soils.

Here, we present the first REE assessment in soils of the two biggest hydrographic basins (Solimões and Rio Negro) of the Brazilian Amazon biome, to test the hypothesis that under the Andean sediments influence, the Solimões soils would be richer in REEs as compared to the Rio Negro soils. Additionally, we used the concentration data to establish their Quality Reference Values (QRV) for REEs pollution. Furthermore, we examined the existence of enrichment and the potential contamination risks of REEs using different environmental assessment indexes in urban soils of Manaus city, which is most important industrial city of Amazon international biome. Our study present clear understanding of REEs geochemical pattern in Amazon soils, which may contribute to improve a knowledge about REEs pattern in Tropical soils.

MATERIALS AND METHODS

STUDY AREA AND GEOLOGICAL SETTINGS

The Amazon rainforest has an approximate area of 5,500,000 km² and this territory cover part of in nine countries (Brazil, Peru, Colombia, Venezuela, Ecuador, Bolivia, Guyana, Suriname and French Guiana). Approximately 60% of the Amazon rainforest occurs in Brazilian territory in nine different states: Acre, Amapá, Amazonas, Mato Grosso, Pará, Rondônia, Roraima, Tocantins and Maranhão (IBGE, 2019).

The Amazonas State is important due to its huge territory (1,559,149 km²), which borders with five Brazilian States (Acre, Pará, Roraima, Mato Grosso and Rondônia) and three countries (Colombia, Peru and Venezuela), and it is entirely covered by the Amazon biome. The Amazon State presents two types of climate by the Köppen classification: i) Tropical rainforest climate (Af), which has no dry season and ii) Tropical Monsoon (Am), which has a short dry season. The average temperature is 26 ºC, and the annual rainfall ranges from 2200 mm to 3200 mm (Alvares et al., 2013).

The geological setting of the Amazonas State is characterized by an extensive lithological diversity, which includes formations from Phanerozoic and Precambrian periods. The main geologic units is the Amazon Craton, which is composed by a sedimentary formation from the Phanerozoic period, located between the Guiana and the Central Brazil Shields (Reis et al., 2006; CPRM, 2010; Horbe et al., 2019).

The sedimentary formation is divided into four sedimentary basins (Amazonas, Solimões, Acre and Alto-Tapajós) and the rock settings are composed mainly of sandstone, siltstone and claystone, with kaolinite and quartz dominating the mineralogy (Cornu et al., 1998; Dubroeucq e Volkoff, 1998; Mafra et al., 2002; Reis et al., 2006). This sedimentary formation was deposited on a Precambrian rocky substrate composed of granites, gneisses, green shale, diabases and amphibolite, which belong to Guiana Shields and the Central Brazil Shield (Costi et al., 2000; Reis et al., 2006; CPRM, 2010).

Normally, the soils of Amazon Craton are highly weathered and deep; they show low nutrients availability due to the strong weathering conditions and chemical nature of the parent rocks (Dubroeucq e Volkoff, 1998; Nascimento et al., 2018; Souza et al., 2018). The dominant Soil Taxonomy orders in the State of Amazonas are Ultisols, Oxisols and Spodosols of the USDA classification and are approximately equivalent to Acrisols, Ferralsols and Podzols of FAO soils classification, which represents 45%, 26% and 7% of Amazonas territory, respectively (CPRM, 2010).

SOIL SAMPLING

Samples were collected from thirty-two sites from pristine and urban areas in the Amazonas State (Figure 1). In the Solimões river basin, the samples were collected in two layers (0-20 cm and 60-80 cm) from 11 sampling sites. Similarly, in the Rio Negro basin the samples were collected in two layers (0-20 cm and 60-80 cm) from 13 sampling sites. The urban topsoils (0-20 cm) samples were taken from 8 sampling points from Manaus city.

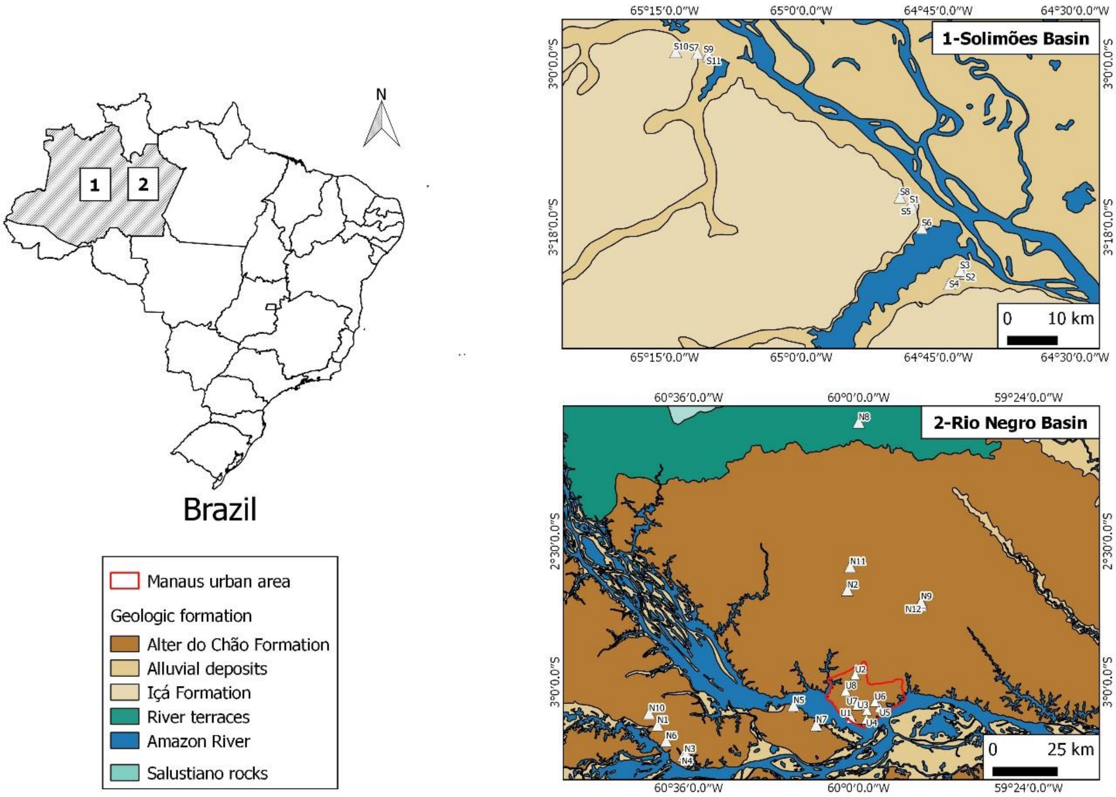

Figure 1: Location of samples collected in Solimões basin (1), Rio Negro basin (2) and Manaus urban area, Amazonas – Brazil.

The soils from pristine areas were collected in areas under natural forest cover whilst the urban topsoil were sampled in areas such as public parks, along the road, residential and industrial areas. The urban sampling sites were chosen based on demographic occupation and the human perturbation level. The urban samples were densely collected near the places with high demographic occupation.

At each sampling point, five individual samples were taken, one collected in a central point and the others collected in each cardinal point. The distance between the central point and each cardinal point was not greater than 10 meters. Due to the different soils classes and different kinds of land use, the pedological horizons features were not considered in the sampling process, which was based on the depth of the sampling layer.

The samples were then homogenized to obtain a composed sample. All the composed samples were stored in polyethylene bags and transferred to laboratory where they were air-dried, ground and sieved through 2 mm sieve.

SAMPLE CHARACTERIZATION

The pH was measured in H_2O and KCl (1 mol L^{-1}) in the 1:2.5 ratio. Particle-size analysis was performed by the pipette method, using NaOH 0.1 mol L^{-1} solution as dispersant and shaking at 50 rpm/16 h describing by Teixeira et al., 2017. The potential acidity (H + Al) was extracted with $Ca(OAc)_2$ 0.5 mol L^{-1} buffered to pH 7.0, and quantified by titration with NaOH 0.0606 mol L^{-1} describing by Teixeira et al., 2017. Exchangeable Ca^{2+}, Mg^{2+}, Al^{3+}, K^{+}, P and P-Rem were measured according to the procedure described by Teixeira et al. (2017). The crystalline and poorly crystalline forms of Fe and Al were extracted by dithionite-citrate-bicarbonate (DCB) buffer solution (Mehra e Jackson, 1960) and oxalic acid-ammonium oxalate (OX) (Schwertmann, 1964), respectively. All analyses were performed in triplicate for each soil sample.

The average Al-isomorphic substitution (IS) of Fe oxides were calculated based the moles of Fe and Al extracted with DCB and oxalate, adapting the (Fontes e Weed, 1991) procedure:

$$\text{IS (\%)} = \left[\frac{(AlDCB - Al\ oxalate)}{(AlDCB - Al\ oxalate) + (FeDCB)}\right] \text{ x } 100$$

X-ray diffraction was used to examine the minerals in clay fraction (< 2 µm) (Moore e Reynolds Jr., 1997). The clay samples were prepared using oriented method; if 2:1 mineral were present, the samples were treated by Mg-saturation, ethylene glycol + Mg, K-saturation at room temperature and heated at 350 ºC and 550 ºC (Whittig e Allardice, 1986; Moore e Reynolds Jr., 1997).

X-ray diffraction analyses were performed with a cobalt tube (λ=1.79026) and Fe filter, operating at 40kV and 30 mA. The scans were carried out in a step-by-step mode in the 4 to 50 º2θ range with 0.05 º2θ of increment and 2 seconds counting time at each step.

SAMPLE DIGESTION PROCEDURE AND REES DETERMINATION

For the determination of the REEs, the soil samples were ground and sieved through a 200 mesh screen. Then, 0.5000 g of each soil sample was digested in a microwave oven using 9 mL of high purity HNO_3 and 3 mL of high purity HCl according to USEPA (1998). After digestion, the extracts were filtered and transferred to 50 mL polyethylene flasks; the volume was filled with ultrapure water (Milipore Direct-Q System).

The rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y and Sc) concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS Perkin Elmer, NexIon 300D). The acid digestion procedures were performed in triplicate.

The eleven-point calibration curve was prepared from a 10 000 mg L^{-1} standard solution for each element analyzed; the correlation coefficient (R) was better than 0.998 for all elements. The isotopes were selected as a function of their natural abundance and spectral interference possibility. Re-calibration was performed when the standard deviation between blank measurements or checkpoint (2.0 µg L^{-1}) measurements were >10%. The limit of detection (DL) was for 0.019 µg L^{-1} La, 0.030 µg L^{-1} for Ce, 0.005 µg L^{-1} for Pr, 0.009 µg L^{-1} for Nd, 0.045 µg L^{-1} for Sm, 0.023 µg L^{-1} for Eu, 0.034 µg L^{-1} for Gd, 0.004 µg L^{-1} for Tb, 0.045 µg L^{-1} for Dy, 0.012 µg L^{-1} for Ho, 0.071 µg L^{-1} for Er, 0.008 µg L^{-1} for Tm, 0.054 µg L^{-1} for Yb, 0.024 µg L^{-1} for Lu, 0.004 µg L^{-1} for Y and 0.057 µg L^{-1} for Sc.

The accuracy were evaluated using two standard soil samples (SRM 2710a and SRM 2709a) and addition-recovery experiments. The addition-recovery experiments were carried out using three concentration levels (10 µg kg^{-1}, 30 µg kg^{-1} and 50 µg kg^{-1}) of all elements evaluated in this study. In performing these procedure, two random samples were selected (S9 and N11) and the concentration levels were added, then the samples were digested in triplicate (for each concentration level) according to USEPA (1998) method and subsequently analyzed by ICP-MS.

The recovery rates of REES in certified soil samples ranged from 90% to 102% (SRM 2709a) and from 93% to 105% (SRM 2710a) considering the leachable values (Mihajlovic et al., 2014; Silva et al., 2016; Alfaro et al., 2018). In the addition-recovery experiments, the recovery rates ranged from 95% to 103% (S9) and 98% to 106% (N11) in the three concentration levels added.

NORMALIZATION AND FRACTIONATION OF REES

To examine geochemical signatures, REE concentrations were normalized using continental crust values (CCE) (Rudnick e Fountain, 1995). The normalized values were obtained by the ratio of the element concentration obtained in this study and the corresponding element of CCE. The CCE data were chosen as normalize value due to the similarity with the geological data of Amazon Craton (CPRM, 2010), preventing the underestimation of La and Ce normalized values and, consequently, avoiding misinterpretations.

The presence of Ce and Eu enrichment anomalies were considered when the value of normalized values were higher than 1.0. The depletion pattern of Ce and Eu were considered when the normalized values were lower than 1.0.

The sum of total concentration of lanthanides, Y and Sc (**Σ**REE(Y+Sc)) and the sum of total concentration of lanthanides (**Σ**REEs) were obtained from surface and subsurface layers both in Solimões soils and Rio Negro soils. Similarly, the sum of the lighter REEs (La to Eu) and heavier REEs (Gd to Lu), called as LREE and HREE respectively, were obtained from surface and subsurface layers where determined in each sampling point to investigate the REEs fractionation.

SOIL CONTAMINATION ASSESSMENT

The Enrichment Factor (EF) for REE was calculated, in order to identify the possible additions compared to natural concentration in surface layer, according to Wu et al. (2014), by the following equation:

$$EF = [X_{\text{sample}}/Y_{\text{sample}}]/[Xn/Y_{\text{earth crust}}]$$

where X is the REE concentration in surface of soil (0-20 cm); Xn is the REE correspondent concentration in the earth crust (CCE) (Rudnick e Fountain, 1995); Y is the concentration of normalizer element. Because natural sources extensively dominate the pattern of aluminium (Al) concentration in the studied area, it was selected as normalizing element (CPRM, 2010).

In order to evaluate the possible increase of REEs concentration compared to the geochemical background, the geoaccumulation index (Igeo) was determined for each sampling point, using the equation described by Müller et al. (1979):

$$\text{Igeo} = \log_2 \frac{\text{Cn}}{1.5\text{Bn}}$$

Where Cn is the concentration of the REE in surface (0-20 cm) and Bn is the REE concentration subsurface (60 - 80 cm); 1.5 is a factor of lithological variation related to the geochemical background (Wu et al., 2014). In the case of the urban topsoil, the Bn value was determined using the mean REEs values of subsurface from representative pristine soils.

The degree of soil contamination, as determined by EF and Igeo, was sorted by using five grades according to their classification criteria (Table S1).

The ecological risk by REEs was evaluated using the Potential Ecological Risk Index (PERI) described by Hakanson (1980):

$$\mathrm{PERI} = Ti \times \frac{C}{Cb}$$

where C is the REE concentration in urban topsoil; Cb is the REE concentration in the earth crust (Rudnick e Fountain, 1995); *Ti* is the biological toxicity factor for each REE, using values reported by Wu et al. (2019) and Chen et al. (2020). Wu et al. (2019) recommends the adoption of *Ti* values equal 1 for all REEs, whilst Chen et al. (2020) adopted the following *Ti* values: La = 1, Ce = 1, Pr = 5, Nd = 2, Sm = 5, Eu = 10, Gd = 5, Tb = 10, Dy = 5, Ho = 10, Er = 5, Tm = 10, Yb = 5, Lu = 20, Y = 2. In this study, we compared both the PERI proposed by Wu et al. (2019) from now on called PERIa and the one proposed by Chen et al. (2020) now termed PERIb. The degree of ecological risk, as determined by both PERIa and PERIb, was sorted by using four grades according to Hakanson (1980) and Chen et al. (2020) classification criteria (Table S1).

The soil contamination and the potential ecological risk assessments were performed in soil samples of urban (U1, U2, U3, U4, U5, U6, U7, U8) and two anomalous areas (S5 and N8). We considered as anomalous, areas the ones with REEs concentrations higher than the percentile 90 values for Solimões basin and Rio Negro basin, respectively.

STATISTICAL ANALYSIS

Results were assessed by descriptive statistical such as mean, median, minimum, maximum and coefficient of variation. The REEs concentration, the extractability of Fe (DCB and oxalate) of soil samples were used within a principal component analysis (PCA) in order to investigate the samples distribution pattern. The data distribution of REEs concentration and chemical and physical properties of each basin were tested by Shapiro-Wilk ($p=0.05$). Due to the non-normal data distribution of REEs and soil chemical and physical properties, the correlations were performed by Spearman rank analysis ($p<0.05$). The statistical analysis were conducted utilizing the PAST 4 software (Hammer et al., 2001).

RESULTS

CHEMICAL AND PHYSICAL PROPERTIES

The data of soil particle-size are presented in Table S2 and Table S3. The soils of Solimões basin have a mean clay value of 34.8% ranging from 8.9% to 55%. The sand percentage in Solimões soils ranged from 23.8% to 83.1%, with a mean value of 46.10%. Whereas Rio Negro soils have a mean clay value of 29.3%, ranging from 1.8% to 74.4%. The sand percentage in Rio Negro soils had a mean value of 65.7% and ranged from 15.2% to 97.3%.

Soils in both basins were classified as being highly acidic ($\text{pH}_{\text{Solimões}} = 4.9$ and $\text{pH}_{\text{Rio Negro}} = 4.6$). The mean values of ΔpH were -0.94 and -0.59 of Solimões soils and Rio Negro basin soils, respectively (Table S2). The potential acidity showed high levels in Solimões soils with mean value 5.37 cmol_c kg^{-1} and a maximum value of 8.80 cmol_c kg^{-1}. In Rio Negro basin soils, the potential acidity showed lower mean value (3.07 cmol_c kg^{-1}), though the maximum value was 8.10 cmol_c kg^{-1}, was similar as compared to the Solimões basin. The cation exchange capacities (CEC) were low in both basins, though Solimões soils showed CEC mean value (3.93 cmol_c kg^{-1}) higher than for Rio Negro soils (1.09 cmol_c kg^{-1}). Corg presented an opposite pattern as compared to CEC, with Rio Negro basin showing Corg values higher than soils from Solimões basin. The Corg of Rio Negro basin soils ranged from 0.1 g kg^{-1} to 22.6 g kg^{-1} and mean value 6.2 g kg^{-1}. Corg in Solimões soils had mean value of 0.8 g kg^{-1} and the maximum and minimum values were 3.8 g kg^{-1} and 0.01 g kg^{-1}, respectively (Table S2 and Table S3).

The urban soils presented potential acidity mean value of 2.41 cmol_c kg^{-1} and the CEC presented mean value of 3.35 cmol_c kg^{-1}. The Corg of urban soils showed mean value of 6.40 g kg^{-1} (Table S2 and Table S3).

CLAY FRACTION MINERALOGY

The X-ray diffraction of the clay fraction showed similar patterns for both basins. The clay fraction of Solimões soils is mainly composed of kaolinite, gibbsite and goethite, but few a samples showed the presence of illite. On the other hand, the clay fraction of Rio Negro basin soils showed only kaolinite and gibbsite (Figure 2).

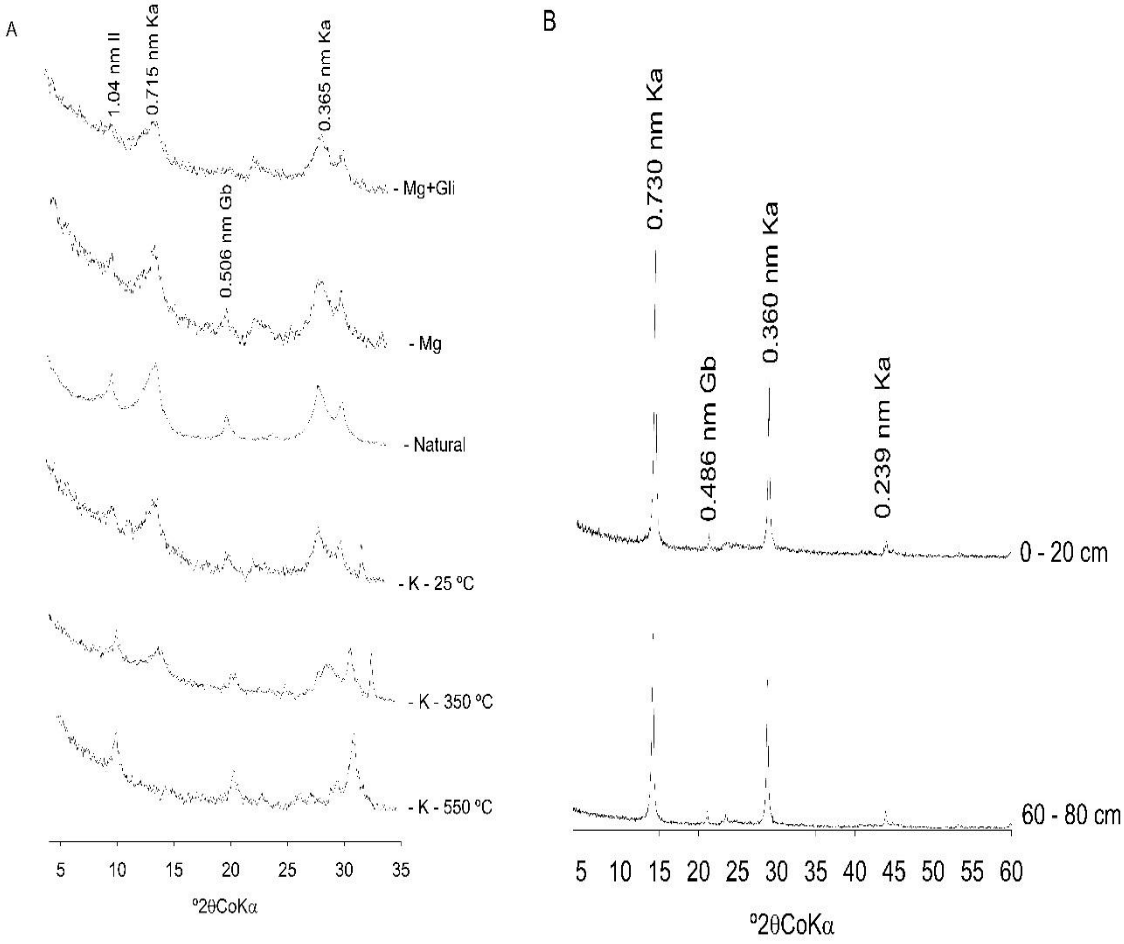

Figure 2: X-ray diffraction patterns of clay fraction from a representative soils of the Solimões basin (A) and Rio Negro basin (B). Ka: Kaolinite; Gb: Gibbsite; Il: Illite.

The values of Fe_{DCB}, Feox, Al_{DCB} and Alox are important measurements for understanding the Fe and Al oxides minerals behavior in the clay fraction of soils and they are used for calculating the Al substitution in the Fe oxides. Their values for the surface and subsurface layers of Solimões and Rio Negro basin soils and for urban topsoils are presented in Table (S1).

The average percentage of Al-isomorphic substitution of Fe oxides in soil samples at surface layer and subsurface layer are presented in Figure S1. The IS values of soils from Solimões basin at surface layer ranged from 12.4% to 37.1%, and the IS mean value was 27.8%. In the soils from Rio Negro basin, the IS values ranged from 4.9% to 73.5%, and the IS mean value was 36.8%. The samples of urban topsoil presented IS values ranged 30.1% to 59.2%, and the IS mean value was 49.6%. In the subsurface samples, the IS values ranged from 16.5% to 38.2% in samples of Solimões basin, while in samples of Rio Negro basin the IS values ranged from 0% to 77.9% (Figure S1).

RARE EARTH ELEMENTS CONCENTRATION IN SOILS

Data from the rare earth elements (REEs) concentrations are presented in Table 1. The REEs mean concentration of Solimões soils varied from 0.07 mg kg^{-1} (Lu) to 42.83 mg kg^{-1} (Ce), whereas in the soils of Rio Negro basin ranged from 0.02 mg kg^{-1} (Lu) to 18.15 mg kg^{-1} (Ce). The REEs mean concentration of urban topsoils range from 0.02 mg kg^{-1} (Lu) to 16.69 mg kg^{-1} (Ce) (Figure 3). The **Σ**REE(Y+Sc) of Solimões soils were higher than the REEs concentration of Rio Negro basin and urban topsoils.

The sum of LREEs averages were 78.09 mg kg^{-1} (0-20 cm) and 72.01 mg kg^{-1} (60-80 cm) in Solimões basin, 33.26 mg kg^{-1} (0-20 cm) and 29.18 mg kg^{-1} (60-80 cm) in Rio Negro basin and 32.44 mg kg^{-1} in urban topsoils. The sum of HREE averages were 4.85 mg kg^{-1} (0-20 cm) and 4.60 mg kg^{-1} (60-80 cm) in Solimões basin. In the Rio Negro soils, the HREE were 2.07 mg kg^{-1} (0-20 cm) and 1.68 mg kg^{-1} (60-80 cm) in Rio Negro basin. The HREE of urban topsoils was 1.47 mg kg^{-1} (Table 1).

The REE concentration normalized to the CCE of two layers are shown in Figure S2. The CCE-normalized data of Solimões soils showed enrichment in Ce while the others REEs exhibited a depletion pattern. In Rio Negro basin soils and urban topsoils, the CCE-normalized data showed depletion pattern of every REEs

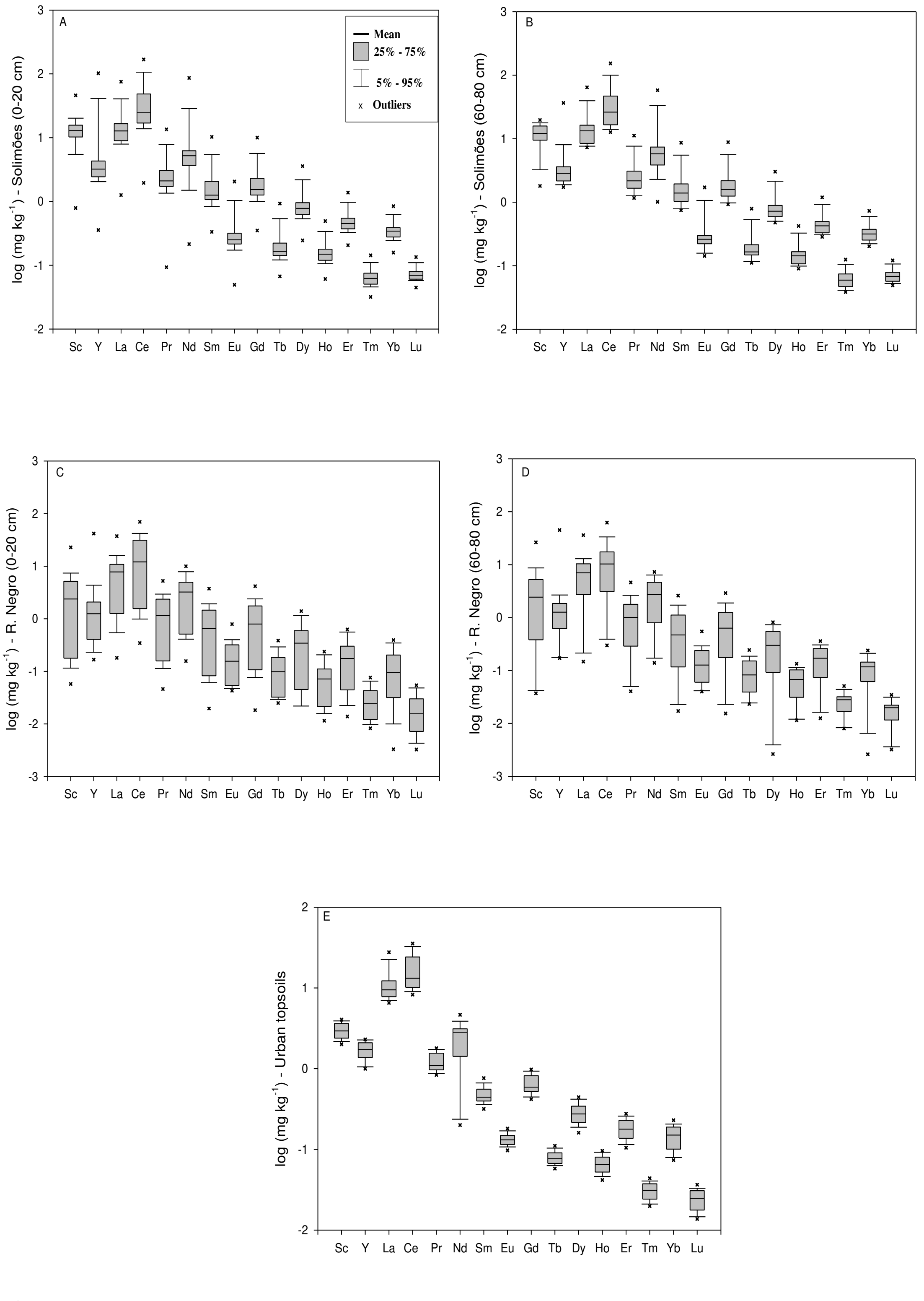

Figure 3: Rare Earth Element concentration in soils from Solimões basin (A and B), Rio Negro basin (C and D) and urban topsoils (E).

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TABLE 1: Mean REE concentrations (mg kg^{-1}) in soils of Brazilian Amazon compared to international soil data and earth crust.

Element (mg kg^{-1})	**Solimões basin[1]**		**Rio Negro basin[1]**		**Urban topsoil[1]**	**Brazil[2]**	**Cuba[3]**	**China[4]**	**Europe[5]**	**Crust[6]**
	0-20 cm	**60-80 cm**	**0-20 cm**	**60-80 cm**	**0-20 cm**					
Sc	14.34	12.23	4.17	3.96	2.97	11.58	-	-	-	30.00
Y	12.01	5.28	4.46	3.58	1.74	17.83	-	-	-	20.00
La	17.71	16.42	9.09	8.51	11.56	20.80	15	37.4	25.9	18.00
Ce	42.83	40.09	18.15	15.41	16.69	43.50	24.2	64.7	52.2	42.00
Pr	3.24	3.04	1.49	1.30	1.21	9.61	5.03	6.67	6.02	5.00
Nd	11.70	10.03	3.39	3.06	2.36	17.70	17.1	25.1	22.4	20.00
Sm	2.18	2.05	0.93	0.74	0.48	3.37	4.4	4.94	4.28	3.90
Eu	0.41	0.39	0.21	0.17	0.13	0.60	0.03	0.98	0.85	1.20
Gd	2.40	2.28	1.07	0.87	0.65	2.32	0.15	4.38	4.2	3.60
Tb	0.24	0.23	0.12	0.10	0.08	0.50	1.21	0.58	0.64	0.56
Dy	1.01	0.94	0.42	0.33	0.29	0.93	1.31	3.93	3.58	3.50
Ho	0.18	0.17	0.08	0.06	0.07	0.17	0.55	0.83	0.72	0.76
Er	0.52	0.50	0.20	0.17	0.18	0.59	2.36	2.42	2.1	2.20
Tm	0.07	0.06	0.03	0.03	0.03	-	0.021	0.24	0.33	0.32
Yb	0.37	0.35	0.13	0.11	0.15	0.67	1.86	2.32	2.09	2.00
Lu	0.07	0.07	0.02	0.02	0.02	0.05	0.77	0.35	0.3	0.33
ΣREE(Y+Sc)	**109.28**	**94.11**	**43.95**	**38.40**	**38.62**	**130.22**	**-**	**-**	**-**	**153.37**
ΣREE	**82.93**	**76.61**	**35.33**	**30.86**	**33.91**	**100.81**	**73.99**	**154.84**	**125.61**	**103.37**
LREE	**78.09**	**72.01**	**33.26**	**29.18**	**32.44**	**95.58**	**65.76**	**139.79**	**111.65**	**90.10**
HREE	**4.85**	**4.60**	**2.07**	**1.68**	**1.47**	**5.23**	**8.23**	**15.05**	**13.96**	**13.27**
LREE/ HREE	**16.10**	**15.65**	**16.06**	**17.40**	**22.07**	**18.28**	**7.99**	**9.29**	**8.00**	**6.79**

1=This study; 2= Sá Paye et al. (2016) and Silva et al. (2016); 3= Alfaro et al. (2018); 4=Wei et al. (1991); 5=Sadeghi et al. (2013); 6=Rudnick and Fountain (1995).

STATISTICAL RELATIONSHIPS

In order to help identify the process that control the distribution of REEs in Amazon soils, Principal Component Analysis (PCA) between REE concentration and Fe-oxides extractability parameters (Fe_{DCB}, Fe_{OX} and IS) of surface layers (Figure 4A) and subsurface layers (Figure 4B) from both basins was performed.

The PCA surface soil results showed that the PC1 and PC2 explained 88.76% of the total variability of the data sets. The first component contributed 57.43% of the total variance and, the variable with highest loading was Fe_{DCB} (0.79). Whereas, the PC2 contributed 31.33% of the total variance and the variable with the highest loading was Ce (0.61).

Similarly, the PCA subsurface results were mainly explained by PC1 and PC2, which together account for 89.24% of the total variability of the dataset. PC1 described 59.67% of the total variance, with Fe_{DCB} (0.91) providing highest positive loading in this component. The second component was strongly loading by Ce (0.81) and explained 29.57% of the total variance.

The correlation matrices were calculated to examine the relationship between the REEs and soil properties The surface layer of Solimões basin showed correlation among most part of REEs, but there were significant correlations ($p<0.05$) only to Sc - SB (ρ=-0.67), Y - SB (ρ =-0.64) and Nd - SB (ρ =-0.79) (Figure S3). The subsurface horizons (60-80 cm) of Solimões soils did not show significant correlations between Sc - REEs, and it negative correlations and between Sc - SB (ρ= -0.66), Nd - H+Al (ρ= -0.67), Nd - CEC (ρ=-0.71) and Nd - Clay (ρ=-0.73) (Figure S6).

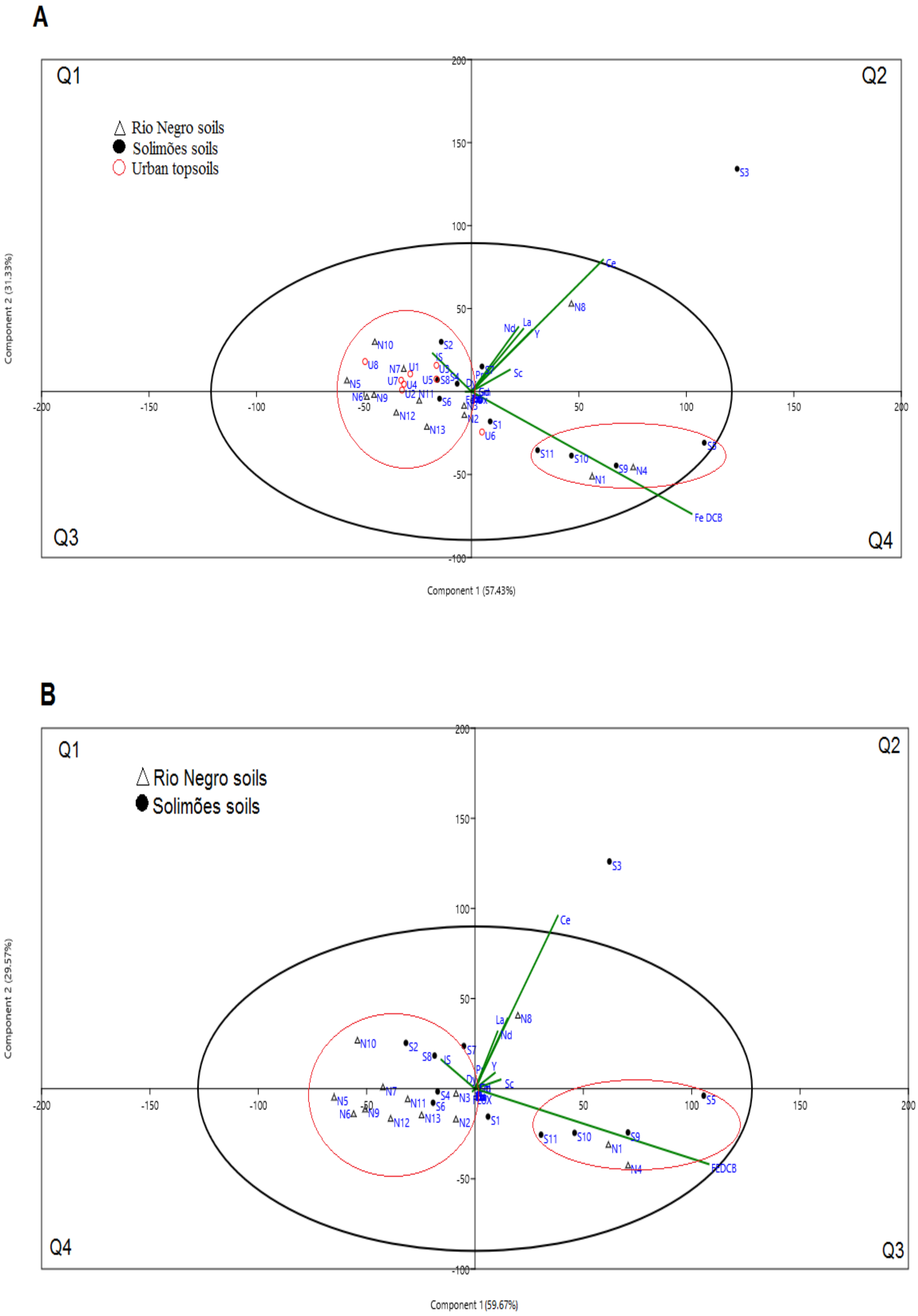

Figure 4: Principal components of REE of surface (A) and subsurface (B) layers for soils from Solimões and Rio Negro basin.

In the Rio Negro soils, the correlation matrix showed similar patterns within the surface (Figure S4) and subsurface horizons (Figure S7). There were negative correlations ($p<0.05$) with the majority of REEs and P-Rem and sand, whereas there were positive correlations between REEs and silt and clay.

In the urban topsoil, the correlation pattern was less consistent compared to the basins, without strong correlations between REEs; Nd did not show correlations with any REEs or chemical and physical parameters. Positive correlations between Sm-CEC ($\rho= 0.77$), Tb ($\rho= 0.82$), Dy ($\rho=0.75$), Yb ($\rho= 0.76$) and Lu ($\rho= 0.87$) were also observed (Figure S5).

SOIL CONTAMINATION ASSESSMENT

Figure 5A shows Enrichment Factors (EF) for REEs in urban topsoils and anomalous areas of Solimões basin (S5) and Rio Negro basin (N8). The Enrichment Factor (EF) values of urban topsoils were smaller than 1, whereas the EF values for the anomalous area in Solimões soils (S5) and Rio Negro mining area (N8) displayed values higher than 1 for several REEs. The soil of the anomalous area of Solimões basin (S5) showed high EF values for Sc (2.13); Y (6.35); La (7.17); Ce (6.82); Pr (4.58); Nd (7.30); Sm (4.44); Eu (2.88); Gd (4.71); Tb (2.82); Dy (1.75); Ho (1.12) and Er (1.10). The soil of the mining area of Rio Negro basin (N8) exhibited EF values higher than 1 for Y (1.83); La (2.09); Ce (1.65); Pr (1.04) and Gd (1.12).

Results of geoaccumulation index (Igeo) are presented in Figure 5B. The Igeo for Tb, Ho, Er, Tm, Yb and Lu showed values smaller than zero for all samples, whereas for Sc, Y, La and Ce they were bigger than 0.

The potential ecological risk index calculated according to Wu et al. (2019), the PERIa, showed low values in all samples for urban topsoils, anomalous areas of Solimões basin and Rio Negro basin (Figure 5C), which ranged from 0.01 (Tm) to 9.59 (Y). Whilst, the PERIb values calculated according to Chen et al. (2020) ranged from 0.01 (Tm) to 34.77 (Lu) in urban topsoils and anomalous areas of Solimões basin and Rio Negro basin (Figure 5D).

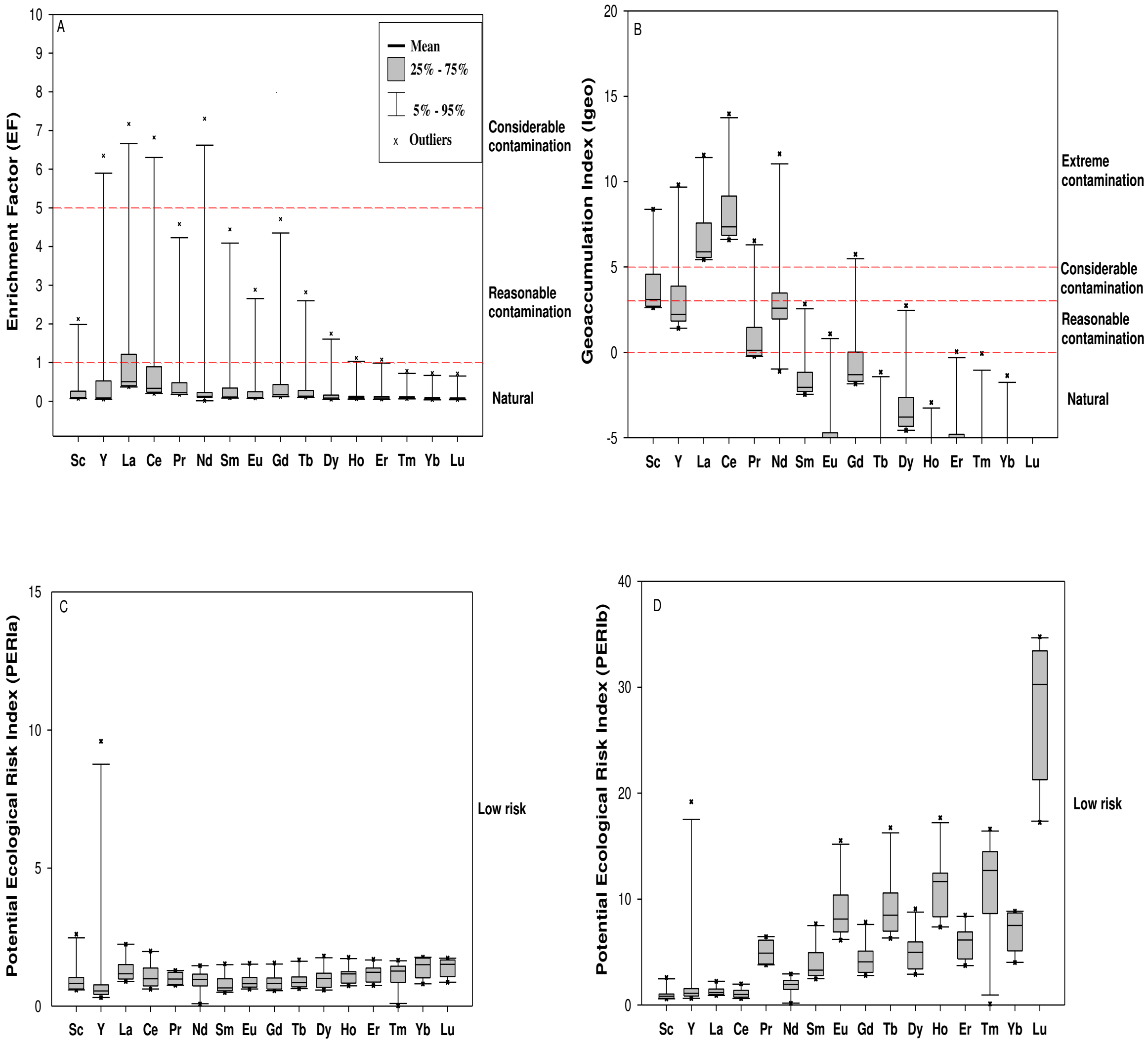

Figure 5: Boxplots diagrams of enrichment factors (EF) (A), geoaccumulation index (Igeo) (B) and potential ecological risk index (PERIa) (C) and potential ecological risk index (PERIb) (D).

DISCUSSION

SOILS CHEMICAL AND PHYSICAL PROPERTIES

Amazonian soils are characterized by high acidity and low nutrients concentration due to the strong weathering conditions resulting from the hot and humid climate that leads to highly developed soils (Cornu et al., 1998; Mafra et al., 2002). The high acidity of Rio Negro soils in comparison to Solimões soils illustrates their hydro-geochemical conditions. Rio Negro basin soils are formed from nutrient poor Pre-Cambrian rocks and are strongly weathered (Cornu et al., 1998; Costi et al., 2009). Additionally, nutrients within the Rio Negro soils undergo intense removal, which are complexed by organic acids and leached from the soil lead to the black water rivers located in Rio Negro basin (Cornu, et al., 1997). The translocation of the organic-metal complexes also results in near-surface sandy horizons (Coomes, 1997; Horbe et al., 2007).

The low acidity and the high CEC of the Solimões soils reflects the geologic signature of the parent material, which were mainly formed by sediments of Phanerozoic (Mafra et al., 2002; Costi et al., 2009; CPRM, 2010). Furthermore, the Solimões basin has received gradual deposition of Andes sediments that contribute to the clay content and CEC increase (Campbell et al., 2006; Horbe et al., 2019). In contrast to the Rio Negro soils, the inputs to the Solimões soils are higher than the outputs, which makes the Solimões basin a rich and fertile soil (Rousseau et al., 2019).

SOIL MINERALOGICAL PROPERTIES

The observed clay mineralogy features of Solimões basin soils suggest important contributions of alluvial and fluvial deposition in the mineralogical properties of these soils. This kind of contribution could explain the occurrence of 2:1 clay minerals in some soils of Solimões basin, especially in soils of low land where the bed rivers influence are more effective (Lima et al., 2006). The contributions of sedimentary materials from Andes through Solimões river have been reported as an important process to maintenance of 2:1 clay minerals in Solimões soils due to the constant input of elements by alluvial and fluvial deposition, mainly during the rainy season (Lima et al., 2006; Viers et al., 2008; Quesada et al., 2010; Guimarães et al., 2013).

On other hand, the contribution of alluvial and fluvial deposition are irrelevant in soils of Rio Negro basin, which result in low mineral diversity in Rio Negro soils (Dubroeucq e Volkoff, 1998). The predominance of kaolinite and gibbsite in Rio Negro basin soils results from the strong weathering action on parent felsic parent material, which results in the destruction of primary minerals and removal of silica necessary for generation or preservation of 2:1 secondary minerals (Cornu et al., 1998; Dubroeucq e Volkoff, 1998; Lima et al., 2006). The strong weathering action in soils of Rio Negro basin is confirmed by the high IS values, which surpassed 33% (goethite limit) in several samples both in surface and subsurface horizons, whereas IS values higher than 33% were rarely noted in Solimões soils.

The IS values of most Rio Negro soils were higher than the IS values observed in other soils of the Amazon biome reported in literature, which normally present IS values range from 0% to 35% (Fritsch et al., 2005; Lima et al., 2006; Damaceno et al., 2020). This pattern suggests that Rio Negro soils were formed in an high acidic conditions that leads to a high activity of Al, resulting in Al incorporation in secondary minerals including iron oxy-hydroxides such as goethite (Fitzpatrick e Schwertmann, 1982; Fontes e Weed, 1991). In addition to the high concentrations of Al_{DCB} in Rio Negro soils, mainly in Spodosols, the presence of other aluminosilicate minerals dissolved during extraction process may contribute to high elevated IS values (Fontes e Weed, 1991; Corrêa et al., 2008). The presence of other aluminosilicates are important contributors to high IS values (>60%) in soils from the northeast region of Brazil, which have high concentration of Al and significant losses of Fe (Lima Neto et al., 2010). Similarly, the IS pattern in Rio Negro soils may be associated to the high Al concentration and the Fe losses during the podsolization process, which could explain the high IS values observed in Spodosols of Rio Negro basin.

CONCENTRATIONS AND PATTERNS OF REES IN SOILS

In general, the **Σ**REE(Y+Sc) and **Σ**REE values obtained in this study were lower than average values found in Brazil, China, Europe and Earth's crust (Wei et al., 1991; Rudnick e Fountain, 1995; Sadeghi et al., 2013; Sá Paye et al., 2016; Silva et al., 2016). However, the **Σ**REE value obtained for soils of Solimões basin was higher than **Σ**REE obtained in Cuba soils by Alfaro et al. (2018). The REEs patterns varied considerably among the different basin and urban areas, with the Solimões basin soils showing consistently higher values as compared to Rio Negro, and in comparison to urban soils. The Solimões basin soils have sedimentary parent material derived from gradual deposition of Andes sediments since the Cenozoic (Campbell et al., 2006). The gradual and recent deposition processes contributed to the formation of clayey and nutrient-rich soils than those of the Rio Negro basin (Basu et al., 1990; Lima et al., 2006; Horbe et al., 2019). During the intermittent deposition cycles that occurred in the geological process of the Içá Formation, the enrichment REEs, as noted within the soils, is considerable (Govin et al., 2014; Horbe et al., 2019; Rousseau et al., 2019).

On other hand, the geology of the Rio Negro basin is mainly composed by fine and medium grained unconsolidated sandstone distributed in discontinuous layers and covered by highly weathered soils (Cornu et al., 1998; Souza e Nogueira, 2009; Silva Carvalho et al., 2014). In addition, the similarity between Rio Negro basin soils and the urban topsoils of Manaus City is expected because it is located almost entirely under the influence of the Rio Negro River (Figure 1).

The different REEs concentration pattern of Solimões soils and Rio Negro soils suggests that the geochemical signature of these basins are a product of a dynamic interaction between geologic features and Andean sediments by rivers action. Several studies have reported the use of elements as tracer in researches about different chemical pattern compositions in rivers of Amazon basin (Bouchez et al., 2010; Guinoiseau et al., 2016; Merschel et al., 2017). It is possible that the use of REEs as tracer in other environmental pools, such as rivers and sediments, could be a powerful tool to understand the degree of physical erosion, the transported sediments amount and their enrichment process in soils at the basin scale. Besides that, the interpretation of REEs indirect data, such as **Σ**REE and LREE/HREE, permit the understanding of geochemical evaluation process as weathering degree and leaching loss (Laveuf e Cornu, 2009).

Our REEs fractionation study showed that the LREE average values in both Rio Negro and Solimões basins comprised around 94% of the **Σ**REE average values, whereas the HREE values were approximately 6% of the **Σ**REE average values (Table 1). This pattern resulted in LREE/HREE ratio values ranging from 15.65 to 22.07 for the soils analyzed, which are higher than the LREE/HREE average values reported in soils from European, Central American and Asian countries (Wei et al., 1991; Sadeghi et al., 2013; Alfaro et al., 2018). The LREE/HREE values observed in this study are similar to the data from Northeast Brazilian soils (Silva et al., 2016), which may suggest a REE fractionation pattern associated to the weathering of the tropical soils. This hypothesis is reinforced by the association of high LREE/HREE values observed in our study with kaolinite and Fe-oxide dominated mineralogy. Several studies have shown that LREE ions can be absorbed by kaolinite and metal oxide surfaces during the weathering process typical in low pH soils, which results in high concentration of LREEs in tropical soils (Li et al., 2014b; Migaszewski e Gałuszka, 2015; Meryem et al., 2016).

RELATIONSHIPS BETWEEN REES CONCENTRATION AND SOIL PROPERTIES

Principal Component Analysis results showed similar patterns for surface and subsurface horizons. In both cases, around 75% of the Rio Negro samples and 90% of Urban topsoil samples were plotted in quadrant 1 (Q1) and quadrant 4 (Q4), which are characterized by low values of Fe_{DCB} and low concentration of REEs, especially LREEs such as La and Ce. The REEs ionic radii characteristics suggest the LREEs, such as La, Ce and Nd, are more easily leached than HREEs in condition of intense weathering (Tyler, 2004; Laveuf et al., 2008), which may explain the depletion of La, Ce and Nd in soil samples both Solimões basin and Rio Negro basin in Q1 and Q4. Additionally, these soils are undergoing continuous eluviation, resulting in low percentage of silt and clay, which further increases the REEs losses (Laveuf e Cornu, 2009).

On other hand, the sample N8 (Q2), which is located in the Pitinga mining zone, showed high levels of REEs and IS values low than 33%. Similarly, samples N1 and N4 (Q3) also showed high levels of REEs and have considerable Fe_{DCB} concentration (>70 g kg^{-1}). The N1, N4 and N8 are Ferralsols and have chemical characteristics similar to Ferralsols from Solimões basin, especially in terms of particle size distribution, percentage of IS and Fe_{DCB} concentration. These patterns suggest the Podzols and Acrisols may be less efficient at retaining REEs (and limiting leaching losses) than Ferralsols due to a combination of eluviation, which can decrease the clay concentration in surface horizons, and less advanced (weathering) clay mineralogy (Laveuf et al., 2008; Laveuf e Cornu, 2009).

The Solimões soils were plotted in Q2 and Q3 and are characterized by high levels of LREEs, especially Ce and La. Soils in Q2 and Q3 showed high levels of Fe_{DCB} concentration (>70 g kg^{-1}) and **Σ**REE(Y+Sc) higher than 60 mg kg^{-1}. Solimões soils that were in Q1 and Q4 have lower REEs concentration (**Σ**REE(Y+Sc) < 60 mg kg^{-1}) and Fe_{DCB} concentration (<70 g kg^{-1}). The predominance of Solimões samples in Q2 and Q3 suggests the key role of Fe-oxides in the REEs distribution. Our findings are consistent with the observation that retention of REEs on Fe-oxides limits REE leaching losses, especially LREEs (Chang et al., 2016).

In terms of soil texture, sandy soils normally have low levels of REEs concentration as compared to clayey soils, the existence of significant correlation between REEs and finer particles indicate the strong adsorption of REEs on minerals through hydroxyl-hydrated sites (Laveuf e Cornu, 2009; Chang et al., 2016). In subsurface samples of Rio Negro soils, all REEs showed positive correlation with clay concentration, which suggest the importance of this adsorption mechanism to mitigate the losses by leaching, especially in sandy soils (Laveuf e Cornu, 2009; Aide e Aide, 2012). The high correlation between REEs in Solimões soils and Rio Negro soils is associated to geologic natural pattern, thus the REEs occur in the same ore deposits (Laveuf et al., 2008). On other hand, the lack of correlation of some REEs and the absence of correlation between Nd and chemical and physical parameters in urban topsoil, as well the presence of positive correlation between REEs with CEC suggest the existence of unnatural pattern. The high correlation of REEs with CEC have been reported as an indicative of REEs enrichment in soils (Chang et al., 2016).

SOIL CONTAMINATION ASSESSMENT

ENRICHMENT FACTOR (EF)

The Enrichment Factor (EF) values of urban topsoils were classified as natural, i.e., without anthropic increases. On the other hand, the EF values for the anomalous area in Solimões soils (S5), located in a pristine area, and Rio Negro mining area (N8), located in an unexplored mining complex area, both displayed values higher than 1 for several REEs (Figure 5A). Sample S5 was collected in an area covered by forest vegetation and negligible human influence; however, this area is located in a low position in the landscape, receiving eroded material from adjacent areas. The sample N8 was collected in an unexplored area of the Pitinga mining complex covered by natural vegetation. The Pitinga Complex has one of the largest REE mineral reserves in Brazil and has particular geological setting composed by calcium-alkaline granite rocks and by volcanic sequences of the Uatumã Group accompanied by clastic and pyroclastic sediments, forming a set of tholeitic hypoabissal sills and dikes (Costi et al., 2000, 2009). The high concentration of REEs occur due to both presence of rocks of plutonic origin and occurrence of metasomatic processes (Takehara, 2015).

GEOACCUMULATION INDEX (IGEO)

The geoaccumulation index (Igeo) of Y, Sc, La, Ce and Nd are greater than zero for all urban topsoils and anomalous areas (samples S5 and N8) (Figures 5B). The elements Pr, Eu, Sm, Gd and Dy showed values higher than zero only in samples S5 and N8. The natural environmental characteristics and the minimum anthropic influence on samples S5 and N8 support the hypothesis that the high values of Igeo in these areas are a result of natural processes. Monitoring of regions where S5 and N8 were collected is highly recommended, since those areas with natural enrichment of REEs can present high levels of bioaccumulation of these elements in plants (Cunha et al., 2012; Liang et al., 2014).

High Igeo values of REEs, especially La and Ce, in urban soils, have been reported (Wu et al., 2019). The origin of REEs are likely electronic boards, vehicular components, rechargeable hydride batteries, and oil industry tools (Zhang et al., 2001; Sun et al., 2017; Pagano et al., 2019; Shin et al., 2019).

POTENTIAL ECOLOGICAL RISK INDEX (PERI)

Using the method proposed by Hakanson (1980), with values for biological toxicity factor (*Ti*) from Wu et al. (2019), the PERIa values obtained in this study were classified as low risk for all analyzed samples. Thus, the REE concentration of the soils do not represent a significant risk to the ecosystems. The results showed that the PERIa classification agree with data obtained by Wu et al. (2019), whom assessed REEs ecological risk in soils of Tibet. According to these authors, one of the biggest concerns with the adoption of a single value for biological toxicity factor for many REEs is the possibility of underestimating the risk to ecosystems. In order to avoid underestimation of risks, we also used the *Ti* values proposed by Chen et al. (2020) for each REEs. The comparison between the results obtained in PERIa and PERIb showed the PERIb values were at least two times higher than PERIa values, although both PERIa and PERIb results had been classified as low risk. The PERIb results were also classified as low ecological risk on the basis of the scales proposed by Hakanson (1980) and Chen et al. (2020). The use of PERIb has the potential to mitigate the underestimation effects in the ecological risks and can give accurate results (Chen et al., 2020).

QUALITY REFERENCE VALUES (QRV): AN INITIAL APPROACH

Since 2009, the Brazilian National Environmental Council, Portuguese acronym CONAMA, has recommended the determination of Quality Reference Values (QRV) for the prevention of soil contamination/pollution by potential toxic elements in each Brazilian State (CONAMA, 2009). The determination of QRV is essential for ensuring that environmental quality of the region, thus, the QRV should be determined based in the local natural concentration of elements, considering the variation of physical and chemical soil characteristics (CONAMA, 2009).

Currently, there are no data for rare earth elements QRV's in Brazilian soils, though several studies have been reported the toxicity, extent of pollution, and the mobility of these elements in trophic chains affecting plants and animals (Zhang et al., 2000; Ramos et al., 2016; Khan et al., 2017a). The REEs are especially toxic to humans because their ionic radii and coordination numbers are similar to that of essential elements such as Ca and Mg (Pagano et al., 2015a, 2015b). Fast absorption coupled with limited excretion lead to accumulation of REEs within humans (Wang et al., 2017a; Pagano et al., 2019), make these elements potentially harmful pollutants that fall under Brazilian QRV legislation definition (CONAMA, 2009).

The Brazilian environmental legislation recommends QRV for potentially toxic elements should be based on the 75th percentile (P75) or 90th percentile (P90) of the samples group (CONAMA, 2009). Normally, QRVs based on P75 are more suitable for regional backgrounds in region with low pedogeochemical variability and are thus not suitable for large areal coverage (CONAMA, 2009; Fernandes et al., 2018).

On the basis of our analyses, we propose QRV values for REEs in soils from Solimões and Rio Negro basins of Amazonas State. Our work provides an initial step for building QRV values for rare earth elements for the Amazonas State and ultimately the Amazon biome.

Due to the huge territory and the different geochemistry of the Solimões and Rio Negro basins, the QRVs were set up separately for both the pristine soils of both basins (Table 2). In order to avoid overestimating QRVs due to anthropogenic influences, the urban topsoil were not considered in the data set of Rio Negro QRVs. The Rio Negro soils had P75 QRVs that were approximately two-times less than P90. The amplitude of Solimões Basin QRVs were higher, especially for Y and Nd, which yielded P75 values 10X less than for P90. This pattern is likely again associated to the contribution of continual Andes sediments deposition, which have a key role in the distribution of Y and Nd in regions of Solimões basin (Basu et al., 1990; Merschel et al., 2017; Rousseau et al., 2019). However, the soils with anomalous REEs concentrations (>P90), both in Solimões basin and Rio Negro basin, present a low contamination risk to Amazon ecosystem. Thus, we considered the adoption of P90 values as QRV in both Solimões and Rio Negro soils as the most suitable for an initial approach of REEs reference values in Amazonas State soils.

Table 2: QRVs proposed for REEs in soils of Solimões basin and Rio Negro basin for Amazonas State - Brazil.

Elements	**Solimões basin**		**Rio Negro basin**	
(mg kg^{-1})	P75	P90	P75	P90
Sc	15.70	**20.88**	5.16	**7.38**
Y	4.31	**43.83**	2.08	**4.36**
La	16.55	**66.06**	10.85	**15.85**
Ce	48.42	**145.63**	31.16	**41.9**
Pr	3.08	**11.67**	2.36	**2.94**
Nd	6.23	**72.95**	4.94	**7.85**
Sm	2.07	**8.58**	1.46	**1.92**
Eu	0.32	**1.72**	0.32	**0.4**
Gd	2.31	**8.35**	1.75	**2.39**
Tb	0.22	**0.79**	0.18	**0.29**
Dy	0.96	**3.11**	0.59	**1.16**
Ho	0.18	**0.44**	0.11	**0.21**
Er	0.55	**1.22**	0.30	**0.56**
Tm	0.08	**0.13**	0.04	**0.07**
Yb	0.39	**0.77**	0.20	**0.35**
Lu	0.08	**0.13**	0.03	**0.05**

CONCLUSIONS

The soils of the Brazilian Amazon present large variations in REEs concentrations as a result of the dynamic interaction between geologic features, sediments depositions and anthropogenic inputs. The high REEs concentration observed in Solimões soils reflect the intermittent alluvial and fluvial Andean deposition cycles in these soils. On other hand, the deposition contribution are irrelevant in Rio Negro basin and REEs leaching losses are more effective due to sandy texture of these soils. Urban topsoils showed similar REEs concentrations to Rio Negro soils as a consequence of being almost entirely under the influence of the Rio Negro River. The soil contamination assessment show slight enrichment in REEs concentration of urban topsoils as compared to pristine soils of the Rio Negro basin. However, the ecological risk associated to REEs contamination was considered low in urban topsoils. Based on the geochemistry of the Amazonas State soils and the low REEs ecological risk observed in this study, the QRVs recommendations for soils of Solimões and Rio Negro basins should be based on the percentile 90. The recommendation of QRVs may serve as a basis for environmental public policies in order to minimize adverse impacts of REEs contamination in the Amazon ecosystem in the future.

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APPENDIX 1

Table S1: Classification of different soil contamination assessment models.

Class	EF[1]	Igeo[1]	PERI[2]	PERI[3]	Description of classes
1	<1	<0	<150	<110	Natural
2	1 - 5	0 - 1	150 – 300	110 – 220	Reasonable contamination
3	5 - 20	1 - 3	300 – 600	220 – 440	Considerable contamination
4	20 - 40	3 - 5	>600	>440	High contamination
5	>40	>5	-	-	Extreme contamination

[1]Wu et al. (2014); [2]Hakanson (1980); [3]Chen et al. (2020)

Table S2: Chemical parameters of topsoil samples (0-20 cm) from Solimões Basin soils and Rio Negro Basin soils.

	pH	ΔpH	PCZ	P	K	Ca^{2+}	Mg^{2+}	Al^{3+}	H+Al	CEC	Corg	P-Rem	CDW	Sand	Silt	Clay	Fe_{DCB}	Feox	Al_{DCB}	Alox
	H_2O			----mg/dm^{-3}----		-----------------cmol$_c$/ dm^{-3}-------------					g/kg	mg/L	kg/kg	------------%-----------			----------------g/kg--------------			
Solimões Basin																				
Maximum	5.2	-0.5	3.4	6.60	12.00	0.90	0.12	5.71	8.80	5.97	3.80	41.20	0.02	83.1	48.5	55.0	105.84	7.35	29.50	9.44
Mean	4.9	-0.9	2.9	0.46	4.15	0.19	0.02	3.71	5.37	3.93	0.80	14.55	0.01	46.1	19.2	34.8	66.13	1.67	14.67	2.88
Median	4.9	-1.0	2.9	0.10	4.00	0.16	0.02	3.79	5.40	3.99	0.70	13.05	0.01	42.6	16.4	36.1	73.55	0.76	12.76	1.83
Minimum	4.4	-1.3	2.5	0.10	0.00	0.08	0.00	0.99	1.50	1.78	0.00	4.40	0.01	23.8	5.9	8.9	23.66	0.38	6.19	0.68
Standard Deviation	0.2	0.2	0.2	1.33	2.82	0.16	0.02	1.20	1.69	1.12	0.9	8.13	0.00	15.8	11.7	14.6	27.59	2.11	6.66	2.66
Rio Negro Basin																				
Maximum	5.8	0.1	4.6	3.20	12.00	1.53	0.09	3.05	8.10	3.80	22.60	56.80	0.17	97.3	14.5	74.4	118.51	8.78	47.43	18.51
Mean	4.6	-0.6	3.5	0.83	1.23	0.30	0.02	0.76	3.07	1.09	6.20	31.74	0.03	65.7	5.1	29.3	47.14	2.80	19.36	6.81
Median	4.7	-0.5	3.7	0.65	0.00	0.19	0.01	0.64	3.00	0.95	4.30	29.05	0.02	72.5	3.3	18.3	36.79	1.80	18.69	5.29
Minimum	3.8	-1.4	1.4	0.10	0.00	0.12	0.00	0.20	0.50	0.37	0.00	11.10	0.01	15.2	0.1	1.8	2.79	0.29	8.56	1.05
Standard Deviation	0.6	0.5	0.9	0.69	2.72	0.30	0.02	0.59	1.68	0.77	5.20	14.85	0.04	29.0	4.5	26.7	35.38	2.74	10.07	4.87
Urban Soils																				
Maximum	6.8	-0.6	4.7	14.30	20.00	4.02	0.25	1.50	6.40	4.22	9.00	50.00	0.08	82.6	9.2	80.4	70.91	8.42	24.73	5.29
Mean	5.4	-0.8	3.7	4.06	13.00	2.95	0.17	0.20	2.41	3.35	6.40	35.79	0.04	58.0	3.2	38.8	32.56	7.78	20.73	4.68
Median	5.3	-0.8	3.7	2.35	15.00	3.06	0.16	0.00	1.85	3.22	8.20	38.95	0.04	63.2	1.5	35.9	28.57	2.63	20.73	4.68
Minimum	3.7	-1.0	2.6	0.80	3.00	1.10	0.11	0.00	0.30	2.82	1.50	21.90	0.02	17.9	0.5	16.7	7.88	7.91	16.73	4.07
Standard Deviation	0.9	0.2	0.7	4.40	5.21	0.87	0.04	0.53	2.13	0.48	3.20	9.42	0.02	20.9	3.2	20.3	17.71	5.43	5.66	0.87

ΔpH: $pH_{KCl} – pH_{H2O}$; PCZ: (2x pH_{KCl})-pH_{H2O}; CEC: cation exchange capacity; CDW: clay dispersed in water.

Table S3: Chemical parameters of subsurface samples (60-80 cm) from Solimões Basin soils and Rio Negro Basin soils.

	pH H_2O	ΔpH	PCZ	P	K	Ca^{2+}	Mg^{2+}	Al^{3+}	H+Al	CEC	Corg	P-Rem	CDW	Sand	Silt	Clay	Fe_{DCB}	Feox	Al_{DCB}	Alox
				----mg/dm^{-3}----		-----------------cmol$_c$/ dm^{-3}-------------					g/kg	mg/L	kg/kg	------------%------------			----------------g/kg--------------			
Solimões Basin																				
Maximum	5.0	-0.6	3.4	2.40	8.00	0.44	0.05	5.32	8.80	5.48	3.90	41.20	0.01	88.0	52.2	57.7	156.67	13.94	34.16	6.07
Mean	4.9	-0.9	3.0	0.27	3.87	0.17	0.02	3.70	5.36	3.89	0.80	14.87	0.01	46.8	19.6	33.6	74.64	2.50	16.10	2.64
Median	4.9	-1.0	2.9	0.10	4.00	0.15	0.01	3.74	5.40	3.93	0.80	14.00	0.01	41.6	18.2	36.6	67.62	1.16	13.79	1.64
Minimum	4.6	-1.1	2.8	0.10	0.00	0.08	0.00	1.28	1.50	1.78	0.00	5.10	0.01	32.5	4.2	6.2	20.20	0.24	7.61	0.37
Standard Deviation	0.1	0.1	0.1	0.59	2.56	0.09	0.01	1.11	1.71	1.07	1.00	8.32	0.00	15.7	12.7	15.2	44.13	4.07	8.21	2.10
Rio Negro Basin																				
Maximum	5.8	0.12	4.6	1.30	6.00	0.74	0.05	3.05	5.50	3.80	13.20	56.80	0.12	98.4	17.3	81.9	139.87	12.78	49.15	12.64
Mean	4.7	-0.6	3.5	0.66	0.62	0.29	0.02	0.81	2.89	1.12	5.40	30.26	0.03	63.1	4.5	32.4	45.62	3.77	16.04	4.86
Median	4.7	-0.5	3.7	0.50	0.00	0.19	0.01	0.69	2.80	0.88	3.90	26.10	0.02	70.0	1.6	23.9	32.05	1.90	12.73	4.68
Minimum	3.8	-1.4	1.4	0.10	0.00	0.12	0.00	0.20	0.50	0.39	0.00	11.10	0.01	9.6	0.1	1.0	3.46	0.42	3.26	1.23
Standard Deviation	0.6	0.5	0.9	0.41	1.71	0.22	0.02	0.75	1.52	0.90	4.50	15.24	0.03	29.9	5.3	28.4	43.41	4.23	11.50	3.32

ΔpH: $pH_{KCl} - pH_{H2O}$; PCZ: (2x pH_{KCl})-pH_{H2O}; CEC: cation exchange capacity; CDW: clay dispersed in water.

Table S4: Detection limited (DL) for REEs determination procedure by ICP-MS.

Samples	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	µg/L															
Blank	und	0.006	0.005	0.006	0.004	0.006	und	0.019	und	0.010	und	0.003	und	0.003	und	und
Blank	und	0.006	0.010	0.013	0.004	0.008	und	0.019	und	0.010	und	0.003	und	0.003	und	und
Blank	und	0.007	0.012	0.017	0.005	0.009	und	0.019	und	0.010	und	0.003	und	0.003	und	und
Blank	und	0.007	0.011	0.016	0.006	0.009	und	0.020	und	0.011	und	0.004	und	0.004	und	0.001
Blank	und	0.007	0.008	0.012	0.005	0.008	und	0.019	und	0.010	und	0.003	und	0.003	und	und
Blank	und	0.007	0.009	0.015	0.005	0.009	und	0.019	und	0.010	und	0.003	und	0.003	und	und
Blank	0.048	0.010	0.028	0.043	0.004	0.017	0.031	0.004	0.024	0.014	0.030	0.012	0.046	0.010	0.036	0.018
Blank	0.034	0.006	0.020	0.028	0.002	0.011	0.029	0.003	0.022	0.013	0.029	0.012	0.046	0.009	0.035	0.017
Blank	0.033	0.006	0.020	0.029	0.001	0.009	0.029	0.002	0.021	0.012	0.028	0.011	0.045	0.008	0.035	0.016
Blank	0.025	0.009	0.017	0.023	0.001	0.009	0.029	0.002	0.022	0.012	0.028	0.011	0.045	0.008	0.035	0.016
Standard Deviation	0.019	0.001	0.007	0.011	0.002	0.003	0.015	0.009	0.011	0.001	0.015	0.004	0.024	0.003	0.018	0.008
Linear regression slope (LRS)	1.0032	1.0215	1.0737	1.0727	1.0203	1.0069	1.0035	1.1037	1.002	1.0728	1.0038	1.0721	1.0052	1.0726	1.0045	1.0712
DL	0.057	0.004	0.019	0.030	0.005	0.009	0.045	0.023	0.034	0.004	0.045	0.012	0.071	0.008	0.054	0.024

Detection Limit (DL): (3 x Blank Standard Deviation)/ LRS;   und: undetectable

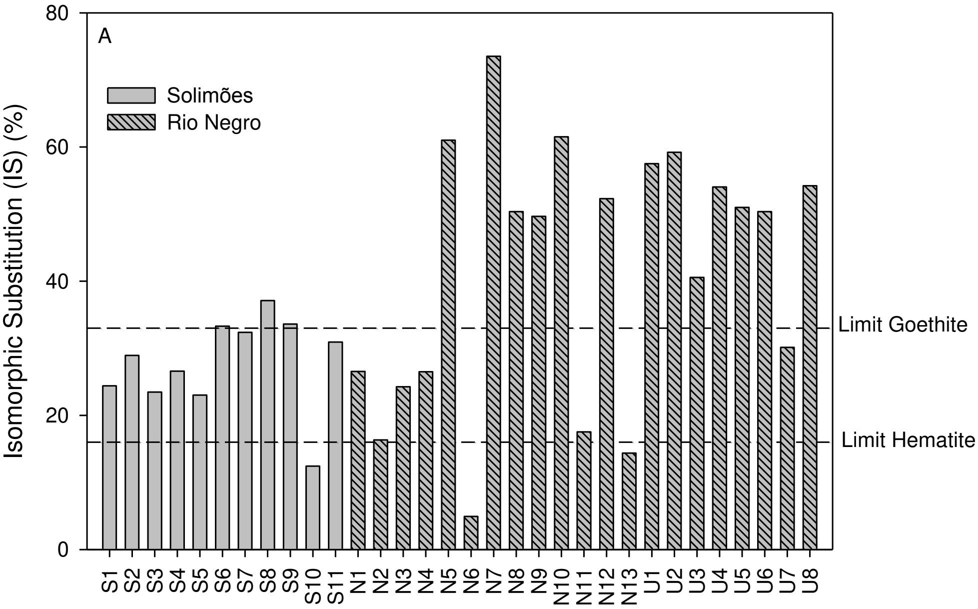
Table S5: Rates recovery of reference material

REE	SRM 2709a*	SRM 2710a*
	%	
Sc	102	105
Y	95	98
La	95	99
Ce	90	99
Pr	95	98
Nd	95	99
Sm	97	101
Eu	97	97
Gd	101	103
Tb	93	100
Dy	ND	99
Ho	93	104
Er	100	99
Tm	ND	ND
Yb	96	93
Lu	101	100

ND: No data in reference material; *See Material and Methods

Table S6: Rates recovery of addition-recovery experiments analyses.

Samples	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	%															
S9 +10 µg/kg	100	102	101	100	100	100	101	99	96	103	97	100	102	102	100	101
S9 +30 µg/kg	100	101	100	98	98	100	100	103	99	101	98	101	104	101	103	101
S9 +50 µg/kg	95	101	104	99	99	100	100	102	99	101	102	101	102	100	102	100
N11 +10 µg/kg	100	99	102	102	109	102	101	100	106	104	103	101	106	102	103	102
N11 +30 µg/kg	106	110	101	103	101	101	104	103	102	102	100	102	105	101	104	101
N11 +50 µg/kg	98	106	104	105	101	101	102	102	101	101	104	101	103	100	103	100



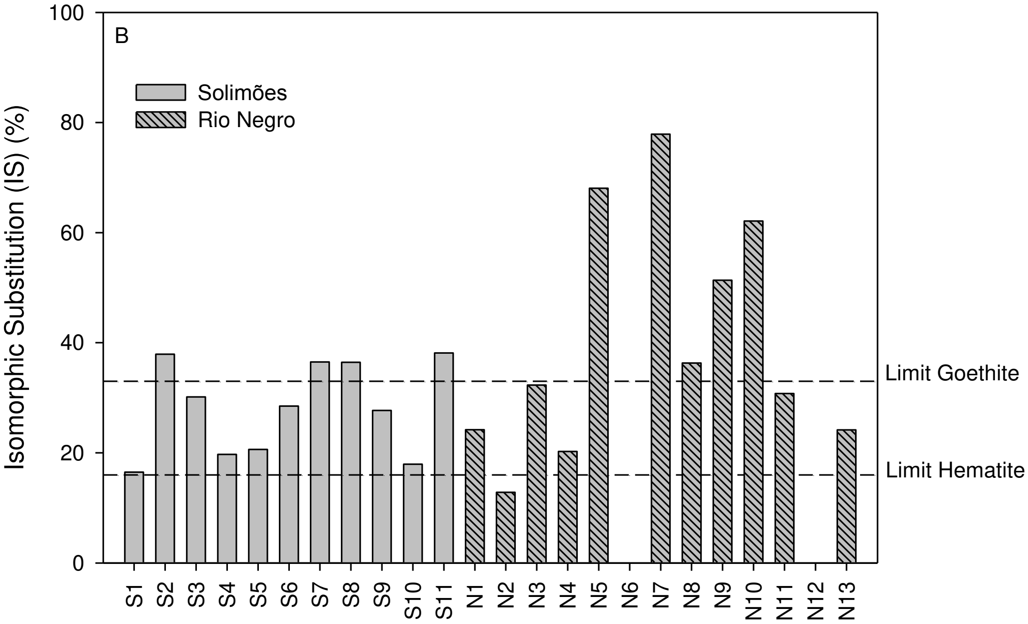


Figure S1: The isomorphic substitution (IS) values in topsoils (A) and subsurface layer (B) of Solimões basin, Rio Negro basin and urban areas.

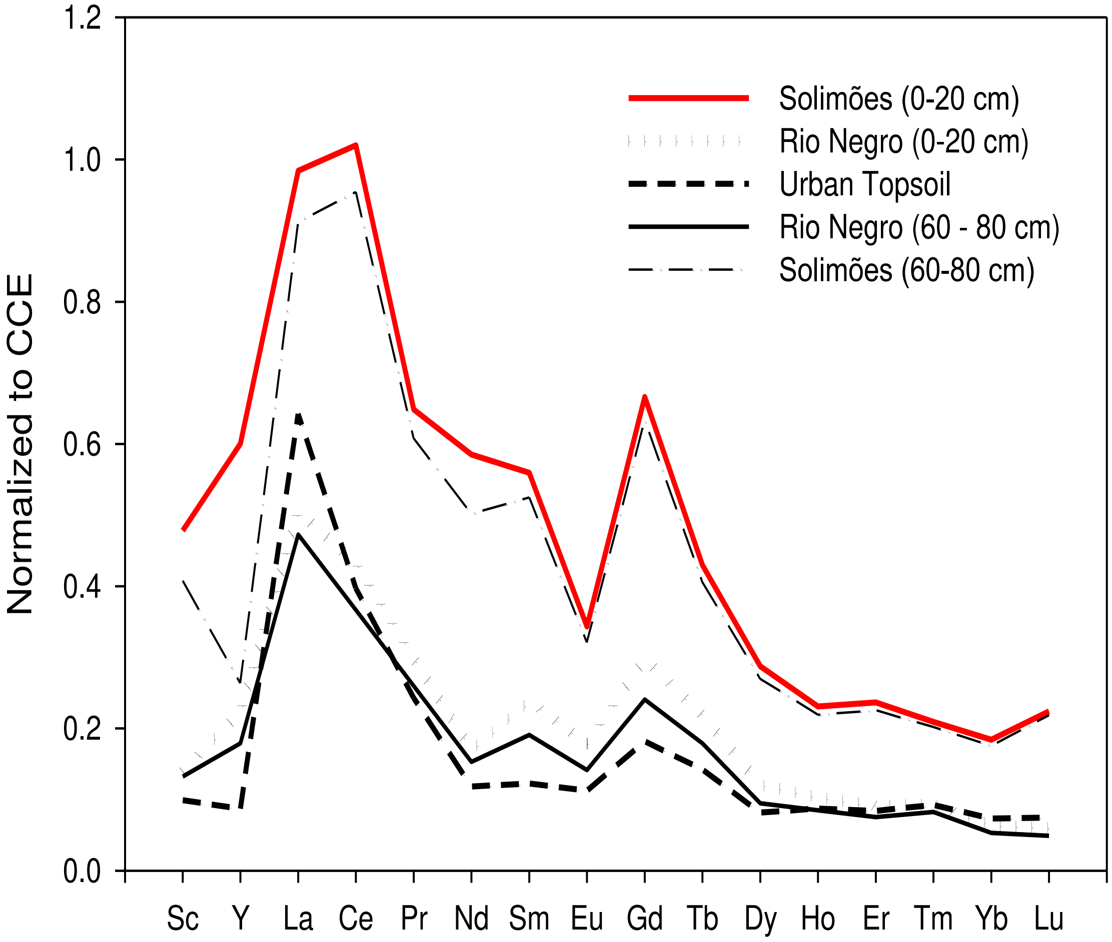


Figure S2: The REE concentration normalized to the CCE (Rudnick e Fountain, 1995) of topsoils and subsurface layers of soils from Solimões basin and Rio Negro basin.

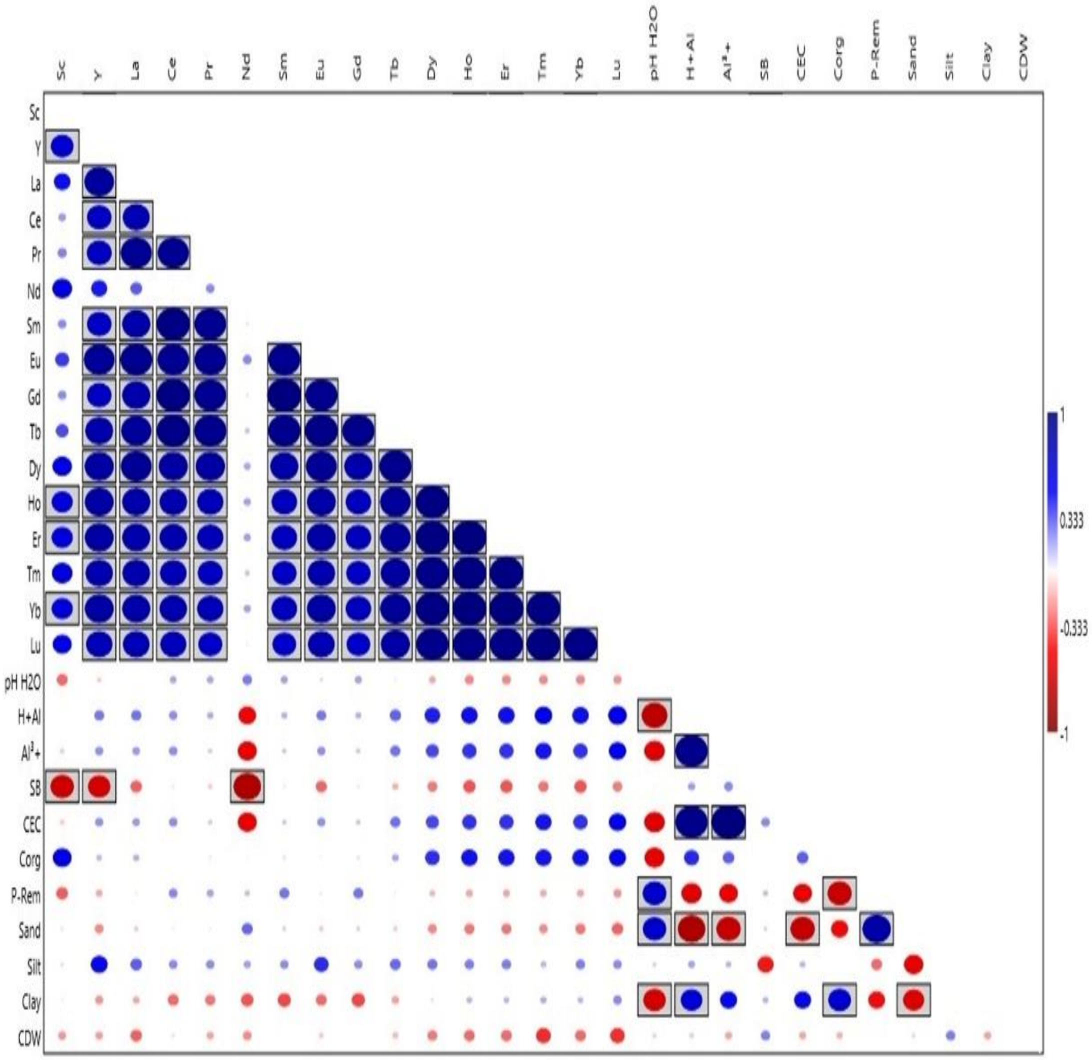


Figure S3: Spearman correlation matrix between rare earth elements (REEs) concentration and soil properties of Solimões soils (0 – 20 cm). Boxed circle means significant correlation ($p<0.05$). Large circles represent higher correlation coefficients. Blue circle: ρ positive value. Red circles: ρ negative value. CEC: Cation exchange capacity; SB: Ca^{2+} + Mg^{2+} + K^{+}; Corg: Total organic carbon; P-Rem: Phosphorous remaining after single sorption; CDW: Clay dispersed in water.

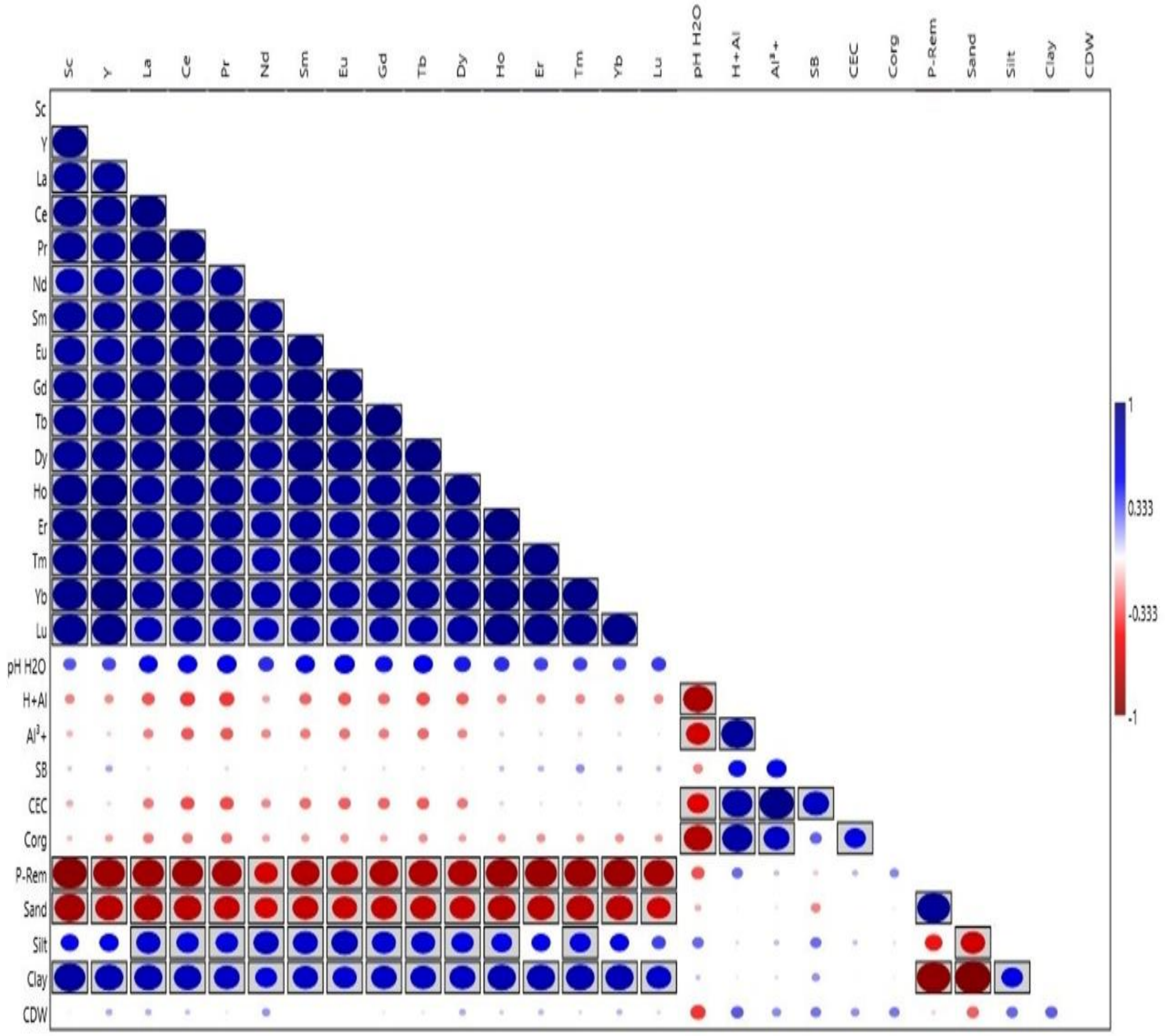


Figure S4: Spearman correlation matrix between rare earth elements (REEs) concentration and soil properties of Rio Negro soils (0 – 20 cm). Boxed circle means significant correlation ($p<0.05$). Large circles represent higher correlation coefficients. Blue circle: ρ positive value. Red circles: ρ negative value. CEC: Cation exchange capacity; SB: $Ca^{2+} + Mg^{2+} + K^{+}$; Corg: Total organic carbon; P-Rem: Phosphorous remaining after single sorption; CDW: Clay dispersed in water.

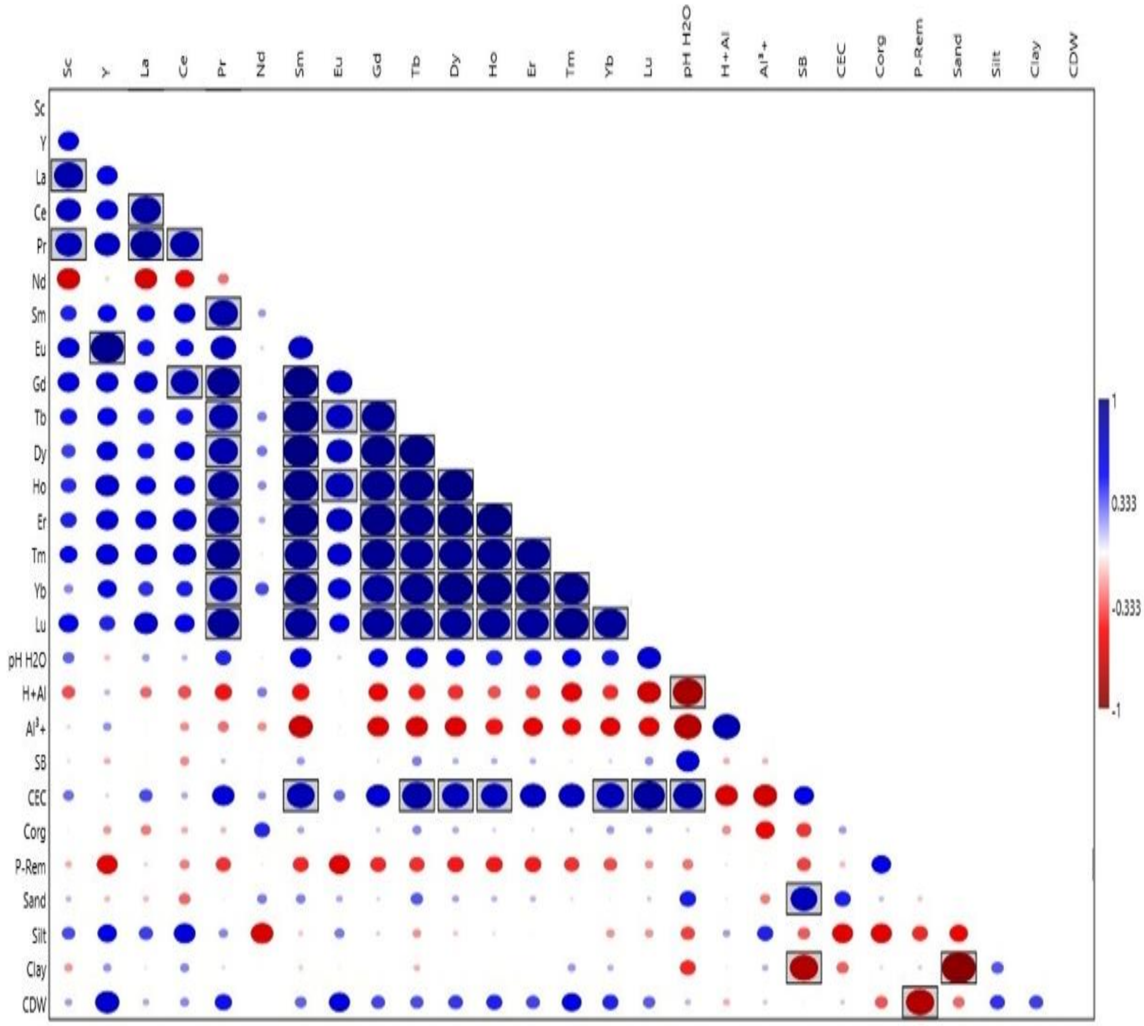


Figure S5: Spearman correlation matrix between rare earth elements (REEs) concentration and soil properties of Urban soils (0 – 20 cm). Boxed circle means significant correlation ($p<0.05$). Large circles represent higher correlation coefficients. Blue circle: ρ positive value. Red circles: ρ negative value. CEC: Cation exchange capacity; SB: $Ca^{2+} + Mg^{2+} + K^{+}$; Corg: Total organic carbon; P-Rem: Phosphorous remaining after single sorption; CDW: Clay dispersed in water.

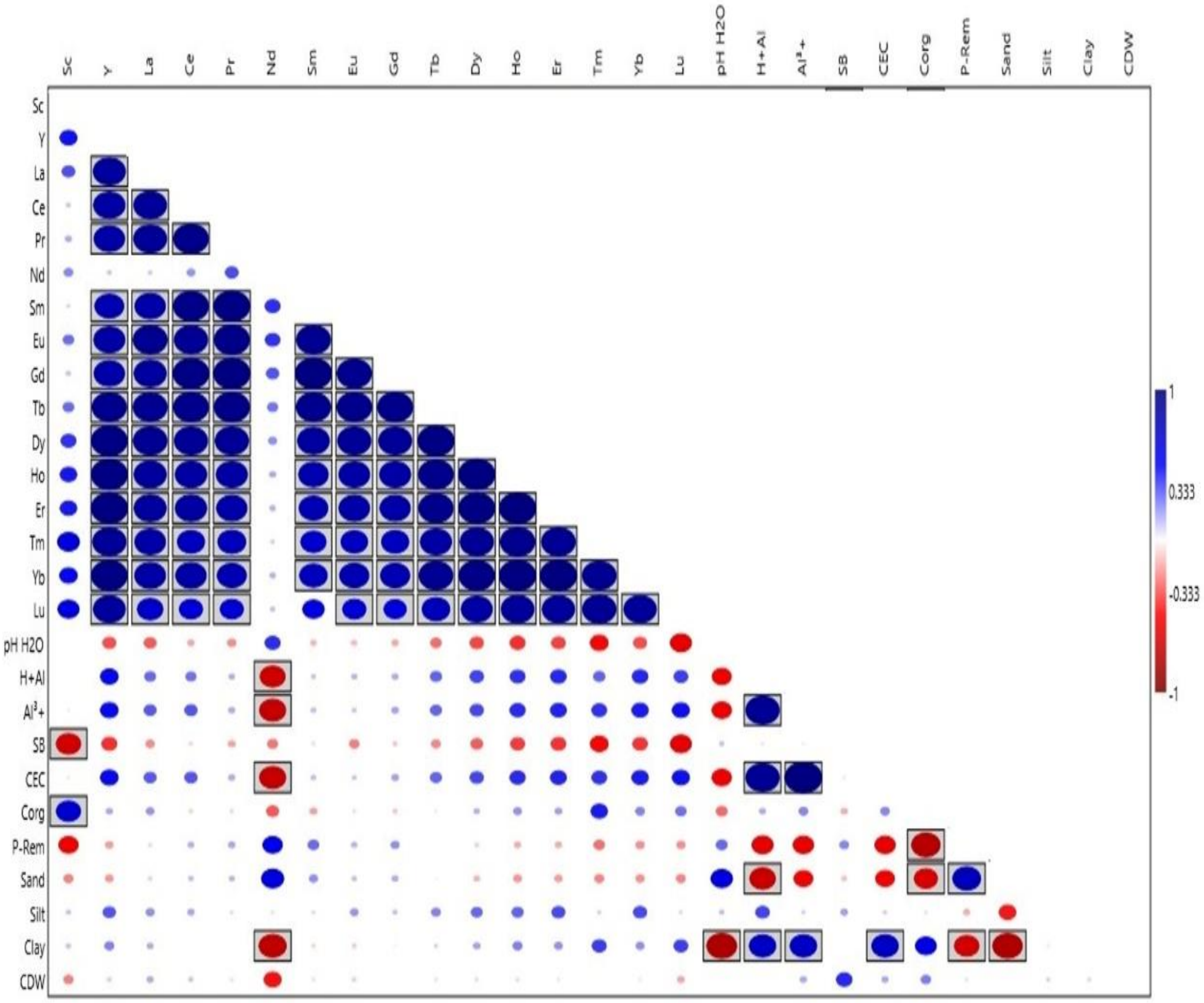


Figure S6: Spearman correlation matrix between rare earth elements (REEs) concentration and soil properties of Solimões soils (60 – 80 cm). Boxed circle means significant correlation ($p<0.05$). Large circles represent higher correlation coefficients. Blue circle: ρ positive value. Red circles: ρ negative value. CEC: Cation exchange capacity; SB: $Ca^{2+} + Mg^{2+} + K^{+}$; Corg: Total organic carbon; P-Rem: Phosphorous remaining after single sorption; CDW: Clay dispersed in water.

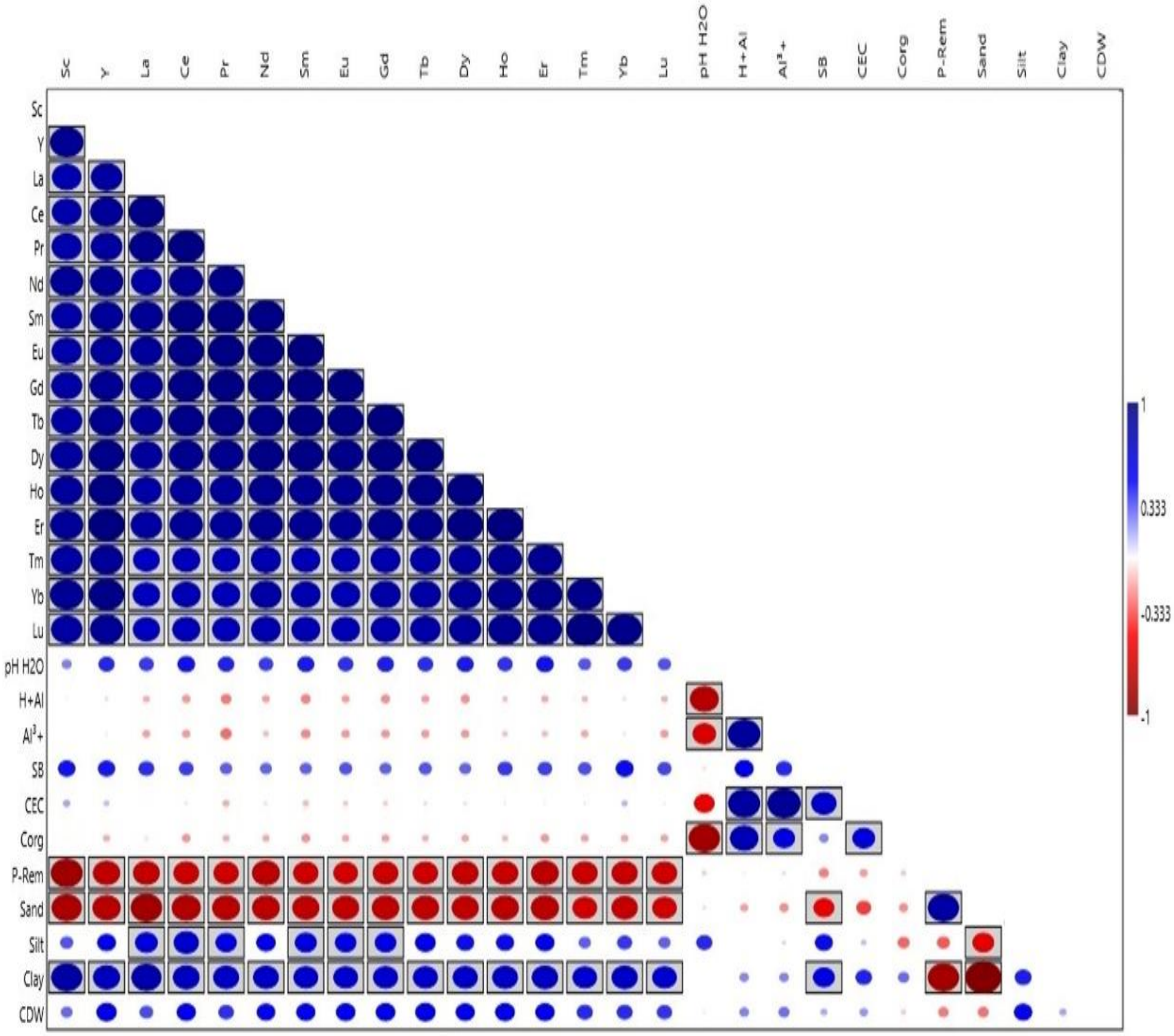


Figure S7: Spearman correlation matrix between rare earth elements (REEs) concentration and soil properties of Rio Negro soils (60 – 80 cm). Boxed circle means significant correlation ($p<0.05$). Large circles represent higher correlation coefficients. Blue circle: ρ positive value. Red circles: ρ negative value. CEC: Cation exchange capacity; SB: $Ca^{2+} + Mg^{2+} + K^{+}$; Corg: Total organic carbon; P-Rem: Phosphorous remaining after single sorption; CDW: Clay dispersed in water.

CHAPTER 2: BIOACESSIBILITY AND GEOCHEMICAL MOBILITY OF RARE EARTH ELEMENTS IN SOILS OF BRAZILIAN AMAZON

ABSTRACT

FERREIRA, Matheus da Silva, D.Sc., Federal University of Viçosa, July, 2021. **Bioacessibility and geochemical mobility of rare earth elements in soils of Brazilian Amazon.** Adviser: Maurício Paulo Ferreira Fontes. Co-adviser: Hedinaldo Narciso Lima.

Rare earth elements (REE) is a term used to group lanthanides (La to Lu) and yttrium (Y) and scandium (Sc) due to their similar chemical properties and the occurrence in the same ores. In the last decades, the economic interest about REE have increased due to the use of these elements in several types of industries such as of high technology, medical and agricultural industries. The exploitation of REE have been followed, in general, by incorrect disposal of tailings and waste, containing REE, in the environment, which makes them be considered as potentially toxic elements in several countries. However, the magnitude of the possible impacts on ecosystem and human health risk caused by REE exposure are relatively unknown, especially in tropical soils. Here, we performed the geochemical characterization, the oral bioaccessible fraction and the health risk associated to exposure of REE in representative Amazon topsoils. We also tested the use of two promising protocols (0.01 mol L^{-1} $CaCl_2$ and 0.43 mol L^{-1} HNO_3) to measure the REE bioaccessible fraction through single extraction. Our findings showed that the bioavailable fractions (exchangeable phase, organic matter phase and Fe/Mn oxides phase) presented low contents and represented less than 20% of the **ΣREE** fraction contents in all the samples. Similarly, the oral bioaccessibility obtained by two *in vitro* methods (Gastric protocol and Gastric-Intestinal protocol) and by the single extraction represented less than 20% of the **Σ**REE fraction contents. The non-carcinogenic risks and the carcinogenic risks associated to REE oral exposure were considerably low for both children and adults in all the Amazon soil samples. The extractions with 0.01 mol L^{-1} $CaCl_2$ showed great potential as a method for measuring the REE bioaccessible fraction in soils with similar condition to soils analyzed in this study.

Keywords: Lanthanides. Sequential extraction. Single extraction. Human exposure. Health risk. Potentially toxic elements

RESUMO

FERREIRA, Matheus da Silva, D.Sc., Universidade Federal de Viçosa, Julho, 2021. **Bioacessibilidade e mobilidade geoquímica de elementos de terras raras em solos da Amazônia brasileira.** Orientador: Maurício Paulo Ferreira Fontes. Coorientador: Hedinaldo Narciso Lima.

Elementos de terras raras (REE) é um termo usado para designar os elementos lantanídeos (La a Lu) e ítrio (Y) e escândio (Sc), que possuem propriedades químicas semelhantes e à ocorrência nos mesmos minérios. Nas últimas décadas, o interesse econômico pelo REE tem aumentado devido ao uso desses elementos em diversos tipos de indústrias, como a de alta tecnologia, médica e agrícola. A exploração dos REE tem sido acompanhada, em geral, pela disposição incorreta de rejeitos e resíduos eletronicos, contendo REE, o que faz com que os REE sejam considerados elementos potencialmente tóxicos em diversos países. No entanto, a magnitude dos impactos sobre o ecossistema e os riscos à saúde humana causados pela exposição aos REE são relativamente desconhecidos, especialmente em solos tropicais. Assim, nesse trabalho realizamos a caracterização geoquímica, a determinação da bioacessibilidade e o risco à saúde associado à exposição de REE em solos amazônicos. Também testamos o uso de dois protocolos promissores (0,01 mol L^{-1} $CaCl_2$ e 0,43 mol L^{-1} HNO_3) para medir a fração bioacessível dos REE por meio de extração única. Nossos resultados mostraram que as frações biodisponíveis (fase trocável, fase matéria orgânica e fase óxidos Fe / Mn) apresentaram baixos teores e representaram menos de 20% dos teores da fração **Σ**REE em todas as amostras. Da mesma forma, a bioacessibilidade oral obtida por dois métodos in vitro (protocolo gástrico e protocolo gástrico-intestinal) e pela extração única representou menos de 20% do conteúdo da fração **Σ**REE. Os riscos não cancerígenos e os riscos cancerígenos associados à exposição oral ao REE foram consideravelmente baixos para crianças e adultos em todas as amostras de solo da Amazônia. As extrações com 0,01 mol L^{-1} $CaCl_2$ apresentaram grande potencial como método de mensuração da fração bioacessível do REE em solos com características similares aos solos utilizados nesse estudo.

Palavras-chave: Lantanídeos. Extração sequencial. Extração única. Exposição humana. Risco de vida. Elementos potencialmente tóxicos

INTRODUCTION

The term Rare Earth Elements (REE) is used to group the inner transition series of the lanthanides, scandium, and yttrium due to their similar chemical properties. The REE have similar atomic radius and are predominantly trivalent (REE^{3+}), although the Ce^{4+} and Eu^{2+} may occur in some environments (Aide e Aide, 2012). Their chemical characteristics permit that REE may substitute for each other in various crystal lattices, which leads to the multiple occurrence of REE in the same ores deposits and consequently, it results in a wide distribution of these elements in the Earth crust. The REE abundance often presents values close to 0.01% to 0.02% and these elements can be found in a huge diversity of minerals such as carbonates, oxides, phosphates and silicates (Loell et al., 2011; Ramos et al., 2016). The only exception is Promethium (Pm) that has a rapid radioactive decay (half-life is 2.62 years), which makes the natural occurrence in the earth's crust virtually impossible (Khan et al., 2017b).

The interest in REE have increased in the last decades due to their use in a number of high tech industries, medical components, and agricultural fertilizers or animals feed-addictive applications (Pagano et al., 2015a). The high demand and the consequent exploitation of REE have been followed, usually, by incorrect disposal of products containing them in soils and rivers, which may represent an elevated risk of environmental contamination (Xinde et al., 2000). The REE have similar pattern to other emergent contaminants, thus these elements can contaminate soils and afterwards, they may be transferred into the food chain (Mihajlovic et al., 2014).

Several works have reported that the no-natural inputs of REE may lead to contamination of soils and the human exposure to these soils may results in several health complications such as respiratory problems and neurological damages (Meryem et al., 2016; Pagano et al., 2019). Additionally, the REE elements can cause cell damage leading to decrease in the total levels of several proteins (Gonzalez et al., 2014). Previous animal studies have shown that the REE exposure can cause adverse effects in terms of inflammation endpoints, oxidative stress, and tissue damage of liver, lungs and kidneys (Pagano et al., 2015a).

Notwithstanding the recent studies, REE's geochemical patterns and their possible impacts on ecosystem are relatively unknown, especially in tropical soils. In Brazil, researches about REE in soils are mainly restricted to determine the total content for establishing natural values of these elements in representative soils of Brazilian regions (Sá Paye et al., 2016; Silva et al., 2016; Pereira et al., 2019; Ferreira et al., 2021a).

However, data of total concentration of elements in the soil should not be the only information to be considered in the evaluation the soils pollution (Li et al., 2014a). The determination of total concentration could provide an initial approach about soils quality but data about chemical mobility and bioaccessible fractionation may provide information about elements mobility and the health risk assessment (Khadhar et al., 2020).

The sequential extraction for speciation of elements bound to different chemical fractions provides information about mobility and availability (Mihajlovic et al., 2014). Normally, sequential extraction provides data about different soil pools such as exchangeable, bound to organic matter and bound to oxides, for example, that could be released to the environment being considered as bioavailable. On the other hand, the elements encased within the crystalline lattices are strongly immobilized and do not represent risk as pollutants (Mihajlovic et al., 2014; Wang e Liang, 2015). Thus, the knowledge about mobilization behavior of chemical elements has a key role to assess the risk potential of soil contamination.

The bioaccessible fraction is defined as fraction of element contaminant that is soluble in the gastrointestinal system (oral bioaccessibility) or lungs (inhalation bioaccessibility) and available for human body absorption (Wang et al., 2017c). The ingestion of soil have been reported as a major route of exposure to many immobile soil contaminants (Oomen et al., 2002).

For this reason, the bioaccessible fraction is normally measured through *in vitro* essays that mimic the effects of gastrointestinal human tract parameters (Drexler e Brattin, 2007; Juhasz et al., 2007). Different *in vitro* essays have been used in assess the bioaccessibility of elements potentially toxics and their health risks because the bioaccessible contents represent an accurately data to assess the potential health risks associated with the ingestion of contaminated soils (Li et al., 2014a).

The use of *in vitro* tests to simulate the gastrointestinal tract requires a long time and use of specific reagents, which are not routinely used in most laboratories (Mingot et al., 2011). In order to streamline and minimize difficulties related to gastro-intestinal essays protocols, the use of single step essays have been reported as a possible alternative (Rao et al., 2010). The use of the of gastric solution as a simplified method to measure bioaccessibility have been reported as excellent alternative to *in vitro* standard methods due to its fast protocol and relative low-cost (Oomen et al., 2002; Pelfrêne et al., 2020). Additionally, other single extractions protocols have been studied to provide more alternatives to bioaccessibility protocols. Among these protocols, the use of unbuffered mild extractors and diluted acid extractors have been reported as a promising alternative due to robustness of their results for different pollutant elements (Rao et al., 2010; Rodrigues et al., 2010a, 2018). However, data about the use of these potential extractors to assess the REE bioaccessibility in tropical soils are unknown.

In this paper, we performed the geochemical characterization, determined the bioaccessible contents and the health human risk associated to exposure of REE (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) in representative Amazon topsoils. Additionally, we tested the hypothesis that REE bioaccessible fraction in those topsoils and their health human risk may be measured by a single extraction using an unbuffered mild extractor (0.01 mol L-1 $CaCl^2$) or a diluted acid extractors (0.43 mol L^{-1} HNO_3).

MATERIALS AND METHODS

STUDY AREA AND GEOLOGICAL SETTINGS

The Amazonas state is the largest state of Brazil, with 1,550,000 km² of territory and have borders with Colombia, Peru and Venezuela. The population of Amazonas state is around 4.2 million inhabitants and more of 52% of the state population lives in the capital of the state (IBGE, 2019). The average temperature in Amazonas state is 26 ºC, the average humidity is 80% and the precipitation levels range from 2200 mm to 3200 mm (Alvares et al., 2013). Two climate types are presented in Amazon State: Tropical rainforest climate (Af) and Tropical Monsoon (Am) (Alvares et al., 2013).

The Amazon Craton is the main geologic unit of Amazonas State. The Amazon Craton is characterized by a large sedimentary cover from Phanerozoic, which is deposited under Precambrian substrate composed by igneous, metamorphic and sedimentary rocks (CPRM, 2010; Horbe et al., 2019). The soils of Amazon Craton normally are formed under strong weathering conditions that favored the bases leaching losses and consequently, present high acidity and low nutrients availability (Cornu et al., 1998; Dubroeucq e Volkoff, 1998). The mineralogical settings of clay are dominated of kaolinite and quartz, although the presence of 2:1 minerals can be noticed in some soils (Cornu et al., 1998; Dubroeucq e Volkoff, 1998). The texture of Amazonas soils may vary from very clayey to sandy, and the occurrence of silty soils are extremely rare (Reis et al., 2006; CPRM, 2010).

SOIL SAMPLES

Twenty topsoil samples (0 – 20 cm) were selected for this study. These samples were collected from natural and urban areas in the Amazonas states (Figure 1). The soils samples were chose in order to represent the major soils class in Amazonas states, which are Podzols, Acrisols and Ferralsols. The sampling was performed according to FEAM (2013), which recommends that each sampling site being composed by five individual samples. Thus, one individual sample was collected in a central point and the others individual samples were collected in each cardinal point. The distance between the central point and the each cardinal point were not upper to 10 meters. Then, the individual samples were homogenized to obtain a composed sample. All the composed samples were stored in polyethylene bags and transferred to laboratory.

SOILS CHARACTERIZATION

The soil samples were air-dried and sieved (2 mm) to remove roots and other materials. Soil pH was measured in 1 mol L^{-1} KCl (pH_{KCl}) and in water solution (pH_{w}) at a ratio of 1:2:5. Particle-size analysis was performed by first reacting soil with 0.1 mol L^{-1} NaOH as dispersant and vertical shaking at 50 rpm/16 h (Teixeira et al., 2017). The sand fraction (2—0.053 mm) was obtained by sieving, and silt was obtained by the difference between clay and sand contents. Exchangeable Ca^{2+}, Mg^{2+} and Al^{3+} were extracted with KCl 1 mol L^{-1} and K^{+} was extracted with Melich-1 extractor (HCl 0.05 mol L^{-1} + H_2SO_4 0.0125 mol L^{-1}). The contents of Ca^{2+}, Mg^{2+} and Al^{3+} were determined by atomic absorption spectrophotometry and K^{+} were determined by flame emission. The sum of bases (SB) was obtained by summing Ca^{2+} + Mg^{2+} + K^{+} exchangeable content and the effective CEC (CEC_e) was obtained by summing SB and Al^{3+}. The potential acidity (H + Al) was measured with $Ca(OAc)_2$ 0.5 mol L^{-1} buffered at pH 7.0, and quantified by titration with NaOH 0.0606 mol L^{-1} (Teixeira et al., 2017).

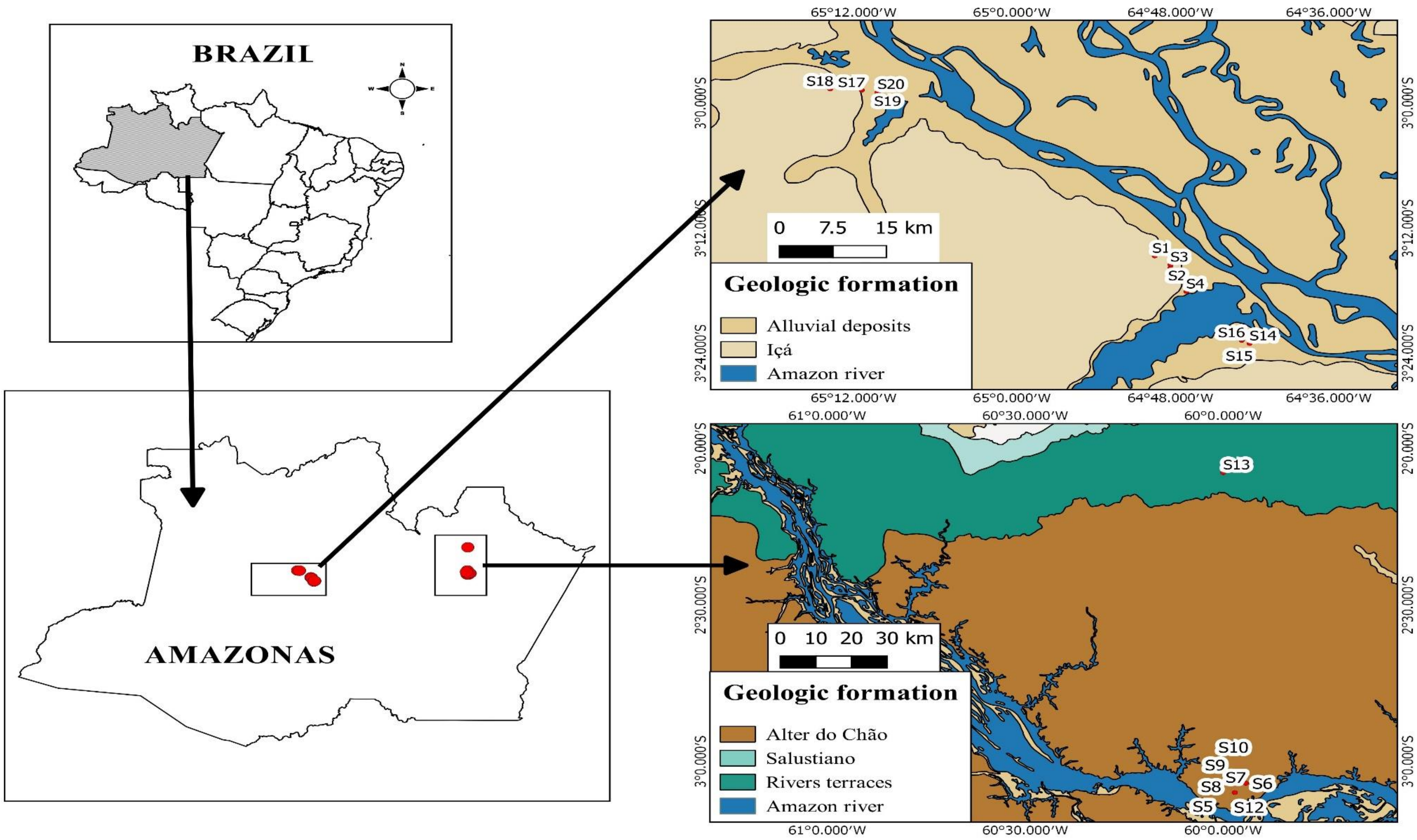


Figure 1: Locations of sampling sites in Amazonas – Brazil.

The CEC_{pH7} was obtained by the summing of SB and potential acidity. Total organic carbon (TOC) was determined by the Walkley–Black method (Walkley e Black, 1934). Remaining P essay (P_{Rem}) was performed by single-value adsorption procedure according to Alvarez et al (2000). The crystalline and poorly crystalline forms of Fe (Fe_{DCB}) were extracted by citrate-bicarbonate buffer solution (Mehra e Jackson, 1960). The poorly crystalline forms of Fe (Fe_{Ox}) was extracted through oxalic acid-ammonium oxalate (Schwertmann, 1964). All analyses were performed in triplicate for each soil sample.

GEOCHEMICAL MOBILITY

The sequential extraction procedure was used to obtain information about the geochemical mobility patterns of REE in the soil samples. The sequential extraction procedure were performed in triplicate and a summary of the extraction (modified Sposito et al., 1982) is described bellow:

1) **Bound to exchangeable phase (BEX):** This fraction of REE was determined by extraction of 1 g of soil (< 2 mm) using 10 ml 0.5M KCl during 16 h continuous shaking (100 rpm) at the ambient room temperature. The extracted solution centrifuged at 6000 rpm for 15 min. The supernatant was filtered through syringe-filter (0.45 µm) and stored at 4 ºC until further analysis.
2) **Bound to organic matter phase (BOM):** This fraction of REE was obtained using the residue of step 1 and 10 ml 0.5M NaOH, the mixture was shaken during 16 h (100 rpm) at the ambient room temperature. The extracted solution centrifuged at 6000 rpm for 15 min. The supernatant was filtered and stored for analysis as the same as the previous step.
3) **Bound to Fe and Mn oxides phase (BOX):** This fraction of REE was obtained using the residue of step 2 and 10 ml 0.05M Na_2EDTA, which was shaken during 6 h (100 rpm) at the ambient room temperature. The extracted solution centrifuged at

6000 rpm for 15 min. The supernatant was filtered and stored for analysis as the same as the previous step.

4) **Bound to residual fraction (RES):** To avoid losses by volatilization the REE concentration associated to the residual fraction was extracted using microwave digestion instead the original procedure preconized by Sposito et al (1982). The residue of step 3 was digested using 9 ml HNO_3 and 3 ml HCl according to EPA 3051a procedure (USEPA, 1998). After, the samples were kept at 4 ºC until further ICP-MS analysis.

SINGLE-STEP EXTRACTION WITH 0.43 MOL L^{-1} HNO_3

For the determination of the REE oral bioaccessibility by diluted acid extractor, the soil samples were previous grinded and sieved at <1 mm. Then, 2.0 g of each soil sample was weighted into a polypropylene bottle and 20 mL of 0.43 mol L^{-1} HNO_3 solution (1:10 soil:solution) were added (Römkens et al., 2009). The bottles were shaken for 2 h at room temperature and then, the extracts were centrifuged (at 6000 rpm for 10 min) and filtered through fine filter paper (0.45 µm pore size). Each extraction procedures were done in triplicate. One blank sample were included in each batch of 10 bottles. All filtrates were stored at 4 ºC until further analysis.

SINGLE-STEP EXTRACTION WITH 0.01 MOL L^{-1} $CACL_2$

The single extraction with 0.01 mol L^{-1} $CaCl_2$ were performed using 2.0 g of each soil sample (<1 mm) and 20 ml of 0.01 mol L^{-1} $CaCl_2$ extraction (1:10 soil:solution) (Houba et al., 2000). The solution and the soil samples were put into polypropylene bottles, which were shaken for 2 h at room temperature and then, the extracts were centrifuged (at 6000g for 10 min) and filtered through fine filter paper (0.45 µm pore size). Each extraction procedures were done in triplicate. The filtrates were acidified with a 1 M HCl solution to prevent adsorption processes and growth of bacteria. The samples were kept at 4 ºC until further analysis.

BIOACCESSIBILITY BY *IN VITRO* DIGESTION

Oral bioaccessibility of REE was estimated using the *in vitro* digestion (IVG) method (Karadaş e Kara, 2011; Boisa et al., 2014). The IVG method has two steps of sequential extraction: gastric and intestinal:

1) **The gastric solution (GS)**: Gastric solution was prepared dissolving 1.25 g porcine pepsin, 0.50 g sodium citrate, 0.50 g malic acid, 420-µL lactic acid, and 500 µL of acetic acid in ultrapure water to a volume of 1 L. The pH was adjusted to 1.5 using concentrated HCl. 0.5 g of each soil sample (sieved at 200 mesh) was weighted and mixed with 50 mL of gastric solution in the reactor vessel, placed in 37 ± 1 °C constant temperature water bath and oscillated at 100 rpm/min, adjusted pH of the solution to 1.5 every 20 min. After 1 h, suspension solution was centrifuged at 3500 rpm for 15 min. The filtrates were stored at 4 ºC until further analysis.
2) **The gastric-intestinal solution (GIS)**: All the procedures of step 1 were repeated. Then, the gastric solution was modified by adjusting the pH to 7 with a saturated $NaHCO_3$ solution followed the addition of 0.087 g bile salts and 0.025 g pancreatin to each reaction vessel. This mixture represented the intestinal digestion solution. After 4 h of digestion by the intestinal phase, the supernatants (gastric and intestinal) were centrifuged (3000 rpm – 1 min) and filtered through fine filter paper (0.45 µm) and the pH solution were adjusted to 2.5. The filtrates were stored at 4 ºC until further analysis.

REE ANALYSIS

The rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y and Sc) concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer, NexIon 300D). The eight-point calibration curve was prepared from a standard solution (10 000 mg L^{-1}) for each element analyzed using the respective matrix, the calibration plot were higher than 0.998 for all elements. The isotopes were selected as a function of their natural abundance and spectral interference possibility. The checkpoint were performed each 15 samples and the blank were performed each 10 samples. The equipment was re-calibrated when the between blank measurements or checkpoint (2.0 µg L^{-1}) measurements >10%. The ICP-MS conditions were optimized using a solution of ^{115}In at 20 ng/ml in 5% HNO_3. An internal standard of ^{115}In at 20 ng/ml was used to compensate for matrix suppression and signal drift during analysis. No matrix matching was necessary due to sufficient dilution (>1:10) of the extracts. The instrument was washed with HNO_3 (1%) between samples during 30 s.

The accuracy and interface effects were evaluated using addition-recovery experiments for sequential extraction and single-step extraction. The addition-recovery experiments were carried out using three concentration levels (10 µg kg^{-1}, 30 µg kg^{-1} and 50 µg kg^{-1}) of all elements evaluated in this study. For performing this procedure, one random sample was selected and the concentration levels were added, then the sample was extracted/digested in triplicate (for each concentration level) and subsequently analyzed by ICP-MS.

The recovery rates of REE in the addition-recovery experiments, the recovery rates of the three concentration levels added are showed in Table S1 and Table S2. Additionally, the sum of the all fractions (BEX + BOM + BOX + RES) obtained by geochemical fraction ranged between 90% to 102% as compared to the data obtained by Ferreira et al. (2021a) about the REE total concentration of the same soil samples utilized in our study, which indicates a fairly good recovery rate. The Limits of Detection are showed in Table S3.

CALCULATIONS OF PERCENTAGE CONTRIBUTION

The percentage contribution of each extraction was calculated according to the following equation:

$$\% = \frac{X}{\Sigma\text{REE fraction}} \text{x } 100$$

Where, X correspond of concentration of HNO_3; $CaCl_2$; GS; GIS and each sequential extraction fraction. The **Σ**REE fraction represents the sum of BEX + BOM + BOX + RES concentrations.

Risk assessment

Human health risks for adults (a) and children (c) were estimated through ingestion exposure (ADD). The ADD was calculated from the following expressions (USEPA, 1989):

$$ADD = \frac{C\ x\ IR\ x\ Ef\ x\ ED\ (a,c)}{Bw\ (a,c) x\ At(a,c)}$$

The values, descriptions and sources of parameters in the formulas are summarized in Table S4.

The non-carcinogenic risk was assessed by the hazard quotient (*HQ*) calculated as the ratio between the environmental exposure dose and the corresponding reference dose (*RfD*) (USEPA, 2002; 2007):

$$HQ = \frac{ADD}{RfD}$$

In the present study, we adopted a unique reference dose value (RfD) for all REE assessment, which was 0.02 mg/(kg x d) (Sun et al., 2017). The *HQ* values below than 1.0 are considered as safe and *HQ* values upper than 1.0 are considered as non-carcinogenic health risk (USEPA, 2004).

The carcinogenic risks were estimated by Lifetime Average Daily Dose (LADD) (USEPA, 2004), as described below:

$$LADD = \frac{C\ x\ EF}{AT}\ x \left(\frac{CR\ (c)\ x\ ED\ (c)}{BW\ (c)} \right) + \left(\frac{CR\ (a)\ x\ ED\ (a)}{BW\ (a)} \right)$$

Then, the carcinogenic risk was calculated using the following equation:

$$Carcinogenic\ Risk = LADD\ x\ SF$$

The Slope Factor (*SF)* used in this study was $3.2\ x10^{-12}$ (Sun et al., 2017).

STATISTICAL ANALYSIS

Results were assessed by descriptive statistical (mean, median, minimum, maximum and standard deviation), Spearman's Rank correlation, linear regression, principal component analysis and cluster analysis (Ward's method with Euclidean distances). All the statistical procedures were carried out with PAST 4.0 software (Hammer et al., 2001).

RESULTS

SOIL PARAMETERS

The pH_{KCl} values ranged from 3.1 to 5.7 and pH_w values ranged from 3.7 to 6.8 (Table S5). The sum of bases (SB) was considered low (< 20 cmolc/dm^{-3}) in most samples and it ranged from 23.6 cmolc/dm^{-3} to 0.1 cmolc/dm^{-3}. The cation exchange capacities (CEC_e) were less than 5.97 cmolc/dm^{-3}. The cation exchange capacities at pH 7 (CEC_{pH7}) ranged from 2.8 cmolc/dm^{-3} to 8 cmolc/dm^{-3}. The TOC presented values below 1.2% in all soil samples. The P_{Rem} values ranged from 4.4 to 50 mg L^{-1}. The data of soil particle-size showed predominance of sand and clay, which present mean values of 50.37% and 37.37%, respectively. The silt percentage in soil samples presented mean value of 12.3%. The values of Fe_{DCB} of soil samples ranged from 7.88 g kg^{-1} to 109.27 g kg^{-1}. The poor crystalline form of Fe (Fe_{Ox}) ranged from 0.38 g kg^{-1} to 8.42 g kg^{-1}.

REE SEQUENTIAL EXTRACTIONS

The mean concentrations of each fraction obtained in sequential extraction were presented in Table 1 and the percentage contribution of each fraction is showed in Figure 2. The average concentration of each REE fraction in ascending order is Bound to Organic Matter (BOM) < Bound to Exchangeable fraction (BEX) ~ Bound to Fe/Mn oxides (BOX) < Residual phase (RES).

In terms of percentage, the contribution of BOM were below 1% in most REE analyzed. The exception of this pattern was the BOM contribution in Sc concentration, which presented 3.37% of Sc concentration bound to Organic Matter fraction (Figure 2a). Exchangeable fraction (BEX) showed contribution below 10% of all REE concentration. Samarium (Sm) was the element with highest BEX contribution (10%) among the REE analyzed in the present study and the lowest BEX contribution was observed for Sc (<1.5%) (Figure 2b).

The percentage of contribution of REE fraction bound to Fe/Mn oxides (BOX) ranged from 1% (Y) to 7.6% (Sc) (Figure 2a). The mean contribution of LREE (La to Eu) bound to Fe/Mn oxides was 5%, whereas the contribution of HREE (Gd to Lu) bound to Fe/Mn oxides was 3.8%. The mean percentage of BOX contribution was 4.3%.

The residual phase (RES) presented high concentrations in all soil samples, the RES contribution ranged from 85.1% (Sm) to 91.3% (Y) and the mean percentage was 90.1%.

1.1 Statistical relationships between soil parameters and REE speciation

In order to investigate the process that control the REE mobility in Amazon soils, the principal analysis components (PCA) was performed among REE concentration in each fraction and soils parameters (Figure 3). The PCA exhibited that PC1 and PC2 explained 83.1% of total variance of data set. The PC1 explained 53.3% of the total variance, the highest loading observed was Sand (0.73). Whilst, the PC2 explained 29.8% of the total variance and the variable with the highest loading was Clay (0.55).

The soil parameters and the sum of all REEs concentrations obtained for each geochemical fraction were submitted to Cluster Analysis according to showed in Figure 4. The data set exhibit two principal clusters: The first cluster include variables such as

Table 1: Mean concentrations of REE in the different extracted fractions of the topsoils samples (0-20 cm) from representative Amazon soils.

Element	**Exchangeable**	**Organic matter**	**Fe/Mn oxides**	**Residual**	**ΣFraction**
	Concentration (mg kg^{-1})				
Sc	0.134	0.347	0.783	9.035	10.299
Y	0.157	0.004	0.097	9.133	9.391
La	0.623	0.010	0.843	15.043	16.518
Ce	2.106	0.021	1.851	30.222	34.200
Pr	0.233	0.002	0.144	2.187	2.566
Nd	0.566	0.006	0.393	6.957	7.921
Sm	0.161	0.001	0.076	1.356	1.593
Eu	0.026	<LD	0.013	0.283	0.322
Gd	0.142	0.001	0.070	1.598	1.810
Tb	0.008	<LD	0.006	0.171	0.185
Dy	0.050	0.001	0.025	0.661	0.737
Ho	0.005	<LD	0.005	0.123	0.133
Er	0.022	<LD	0.014	0.348	0.384
Tm	0.001	<LD	0.002	0.049	0.052
Yb	0.012	0.001	0.011	0.250	0.274
Lu	0.001	<LD	0.003	0.048	0.052
ΣREE	4.248	0.393	4.334	77.464	86.439
Maximum	2.106	0.347	1.851	30.222	34.200
Mean	0.266	0.025	0.271	4.841	5.402
Median	0.092	0.001	0.047	1.009	1.165
Minimum	0.001	0.000	0.002	0.048	0.052
Standard Deviation	0.527	0.086	0.501	8.116	9.114

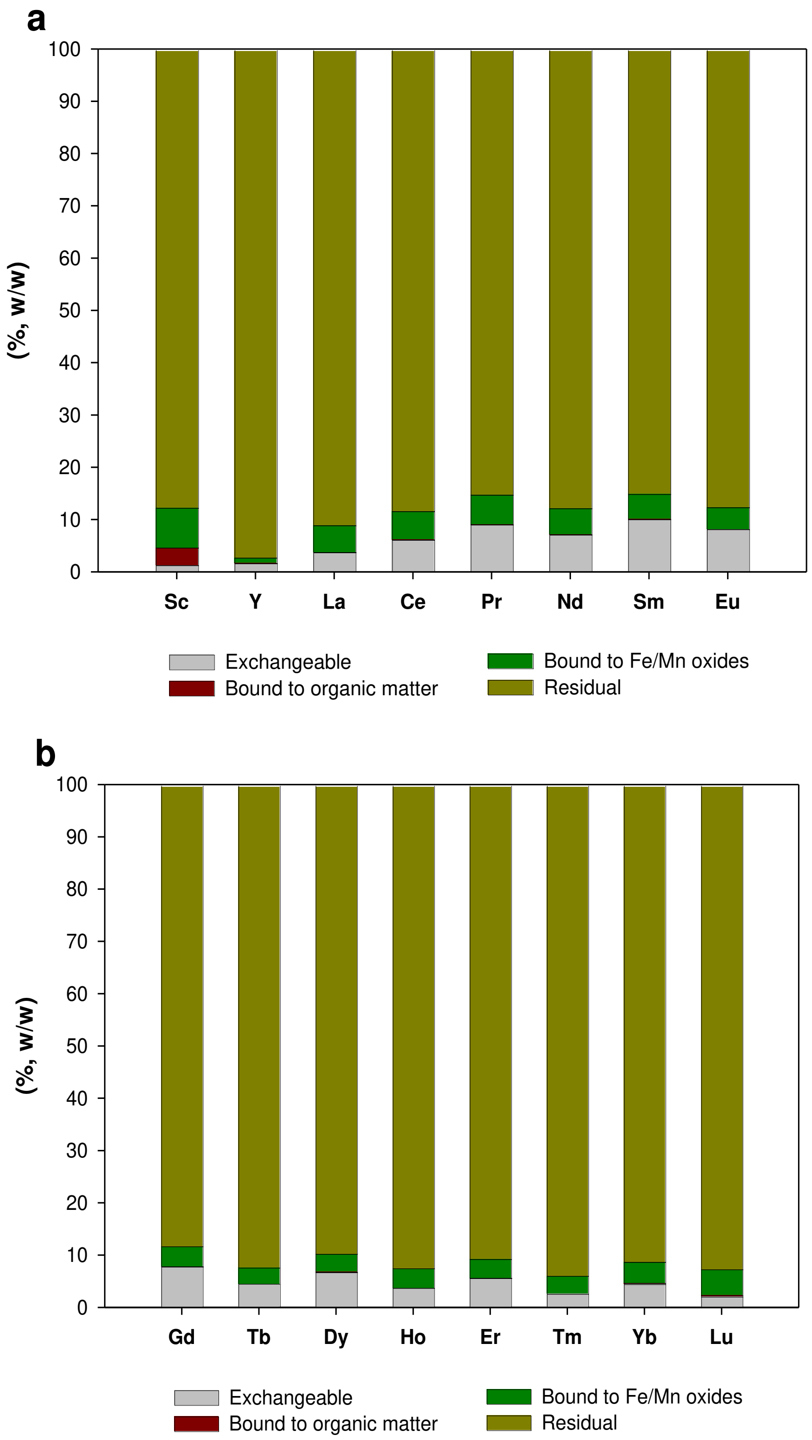


Figure 2: Percentage of each fraction of Sc-Eu (a) and Gd-Lu (b) in Amazonas soils.

Sum BEX, pH_{KCl}, Sum BOX, TOC and Sum BOM. Whereas, the second cluster include only Sum RES and Sand, which were joined at a relatively higher level.

The Spearman correlation ($p<0.05$) matrices were performed to investigate the possible relationship between the REE concentration obtained by different extraction and the soil properties (Figure 5). The correlation matrices exhibited predominance of negative correlation between the Sum BEX, Sum BOM, Sum BOX and the soil parameters. The significant negative correlations ($p<0.05$) were obtained in Sum BEX- pH_{KCl} (-0.68), Sum BEX-SB (-0.80), Sum BEX-TOC (-0.71), Sum BEX-P_{rem} (-0.67), Sum BEX- Fe_{Ox} (-0.77), Sum BOM-SB (-0.59), Sum BOM-Prem (-0.51), Sum BOX- pH_{KCl} (-0.63), Sum BOX-SB (-0.73), Sum BOX-P_{rem} (-0.73), Sum BOX- Fe_{Ox} (-0.64), Sum RES-SB (-0.67) and Sum RES-P_{rem} (-0.45) .

Significant positive correlations were observed between the Sum BEX-Silt (0.82), Sum BOM-Silt (0.45), Sum BOX-Silt (0.79) and Sum RES-Silt (0.60). Whereas, significant negative correlations were noticed only in Sum BOX-Sand (-0.52) and RES-Sand (-0.51). Significant negative correlations were also observed between the single extraction procedure and soil parameter: Sum $CaCl_2$- pH_{KCl} (-0.70), Sum $CaCl_2$-SB (-0.77), Sum $CaCl_2$-TOC (-0.78), Sum $CaCl_2$-Prem (-0.63), Sum $CaCl_2$- Fe_{Ox} (-0.70), Sum GIS- pH_{KCl} (-0.51), Sum GIS-SB (-0.72), Sum GIS-TOC (-0.69), Sum GIS-Prem (-0.60), Sum GIS- Fe_{Ox} (-0.75), Sum GS- pH_{KCl} (-0.46), Sum GS- pH_{KCl} (-0.46), Sum GS-SB (-0.63), Sum GS-TOC (-0.70), Sum GS- Fe_{Ox} (-0.74). The silt content presented significant positive correlation with Sum $CaCl_2$ (0.78), Sum GIS (0.67) and Sum GS (0.58).

The significant positive correlations ($p<0.05$) were noticed to Sum $CaCl_2$- Fe_{DCB} (0.52), Sum $CaCl_2$- Fe_{DCB} (0.52) and Sum GIS- Fe_{DCB} (0.52). Furthermore, the relation between the single extractors ($CaCl_2$, GIS and GS) and the most available phases of sequential extraction (BEX, BOM and BOX) presented significant positive correlation.

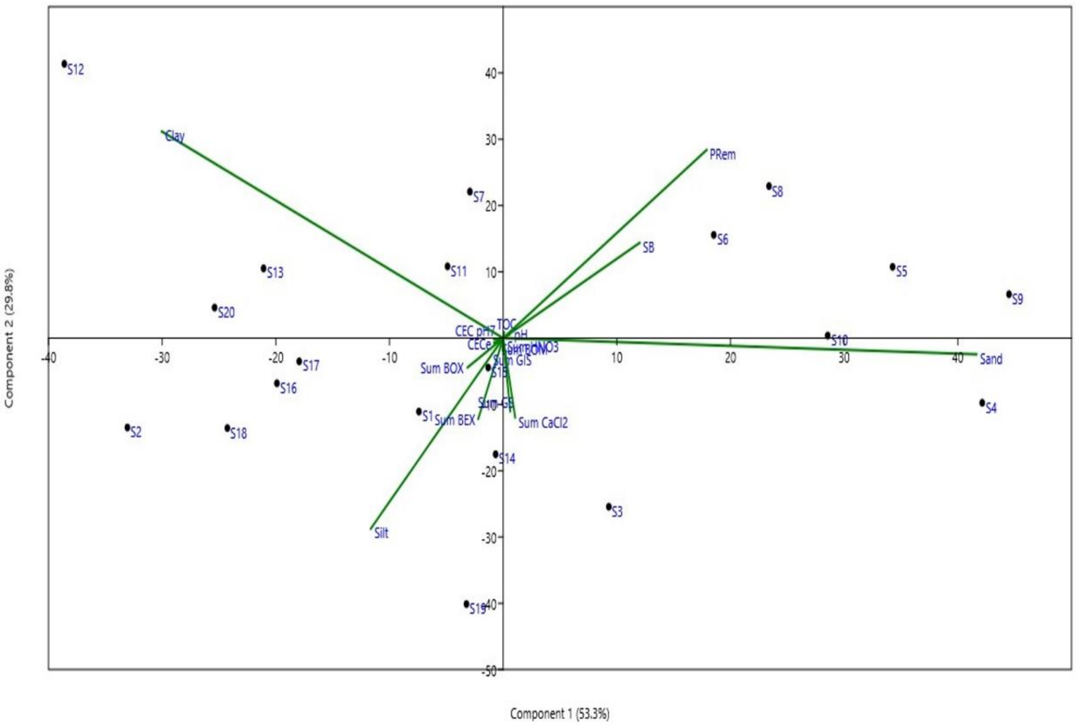


Figure 3: Principal components analysis of REE extractions and chemical properties of soils.

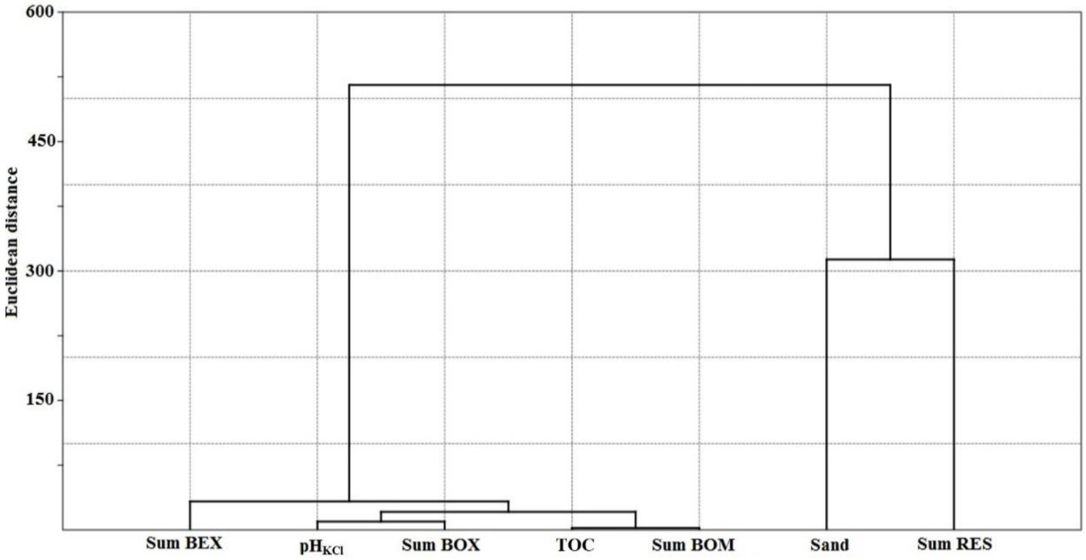


Figure 4: Dendrogram of REEs speciation versus chemical properties of soils. TOC: Total organic carbon; Sum BEX: ΣREEs bound to exchangeable phase; Sum BOM: ΣREEs bound to organic matter; Sum BOX: ΣREEs bound to Fe and Mn oxides; Sum RES: ΣREEs bound to Residual fraction.

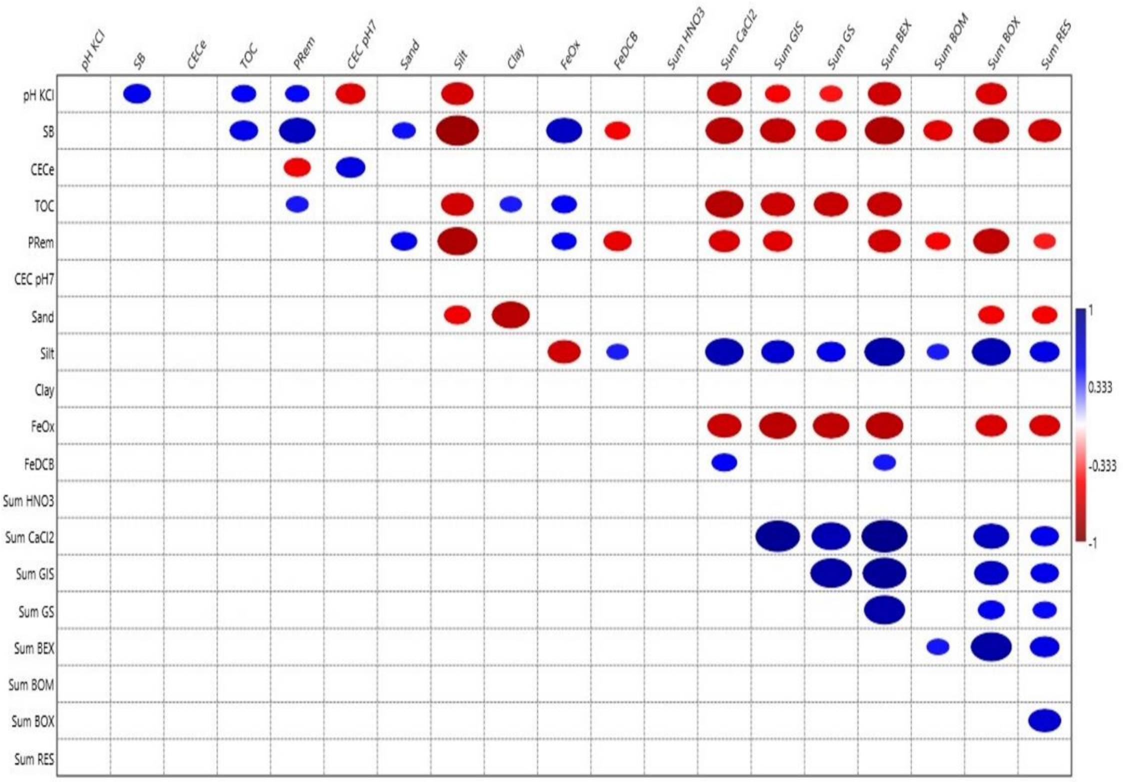


Figure 5: Spearman rank analysis between the sum of rare earth elements concentrations using different extractors and soil properties. Only significant correlation are shown ($p<0.05$); Blue circle: ρ positive value. Red circles: ρ negative value. CECe: Cation exchange capacity; SB: $Ca^{2+} + Mg^{2+} + K^{+}$; TOC: Total organic carbon; PRem: Phosphorous remaining after single sorption; FeDCB: Crystalline and poorly crystalline forms of Fe; FeOx: Poorly crystalline forms of Fe; GIS: Gastric-intestinal extraction; GS: Gastric solution extraction; BEX: REE bound to exchangeable phase; BOM: REE bound to organic matter; BOX: REE bound to Fe and Mn oxides; RES: REE bound to Residual fraction.

SINGLE-STEP EXTRACTION

The REE concentrations extraction with 0.43 mol L^{-1} HNO_3 are presented in Figure 6 and the percentage contribution in relation of ΣFraction are presented in Figure 7. The REE concentrations 0.43 mol L^{-1} HNO_3 extraction ranged from 0.002 mg kg^{-1} (Lu) to 0.48 mg kg^{-1} (Ce) and the mean value extracted was 0.081 mg kg^{-1}. In percentage terms, the 0.43 mol L^{-1} HNO_3 extraction showed values below 2% of percentage contribution for all REE. Only La, Ce, Nd and Gd presented values higher than 1% of percentage contribution.

REE concentrations extraction with 0.01 mol L^{-1} $CaCl_2$ presented values ranging from 0.002 mg kg^{-1} (Lu) to 1.59 mg kg^{-1} (Ce) (Figure 6). The 0.01 mol L^{-1} $CaCl_2$ extraction percentage presented mean values higher than 2% for most soil samples and, some elements (Ce, Sm, Eu, Dy, Er and Yb) showed percentage contribution higher than 20% (Figure 7).

REE BIOACCESSIBILITY CONCENTRATION

In order to determine the REE bioaccessibility concentration, two *in vitro* essays were performed. The first one is based on gastric solution concentration (GS) and the second one is based on gastric-intestinal solution concentration (GIS). Both GS concentration and GIS concentration are presented in Figure 6. The REE concentration obtained through GS essay ranged from 0.002 mg kg^{-1} (Lu) to 0.22 mg kg^{-1} (Y) and the percentage contribution ranged from 0% (Eu, Yb) to 42.9% (Nd) (Figure 7). The REE concentration obtained through GS from 2.5 x10^{-4} mg kg^{-1} (Tm) to 0.24 mg kg^{-1} (Ce) and the maximum percentage contribution observed was 7.1% (Nd).

PREDICTING REE BIOACCESSIBILITIES BY SINGLE-STEP EXTRACTIONS

The results of REE bioaccessibilities prediction for GS and GIS through soil reactive pool extraction are presented in Table 2 and Table 3, respectively. The results exhibited the close match between the concentration of four REE (Pr, Sm, Eu and Gd) extracted with 0.43 mol L^{-1} HNO_3 and the bioaccesible concentration extracted by GS. Whereas, the REE concentration extracted by 0.01 mol L^{-1} $CaCl_2$ showed close match between the GS concentration extracted for 13 REE (Y, La, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu).

The gastric-intestinal (GIS) bioaccessibility prediction using 0.43 mol L^{-1} HNO_3 extractor was satisfactory for Pr, Nd, Sm, Eu and Gd. While, the GIS bioaccessibility prediction by 0.01 mol L^{-1} $CaCl_2$ extraction was satisfactory for 14 REE (Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu).Both 0.43 mol L^{-1} HNO_3 and 0.01 mol L^{-1} $CaCl_2$ extractors could not predict Sc and Ce bioaccessible concentration.

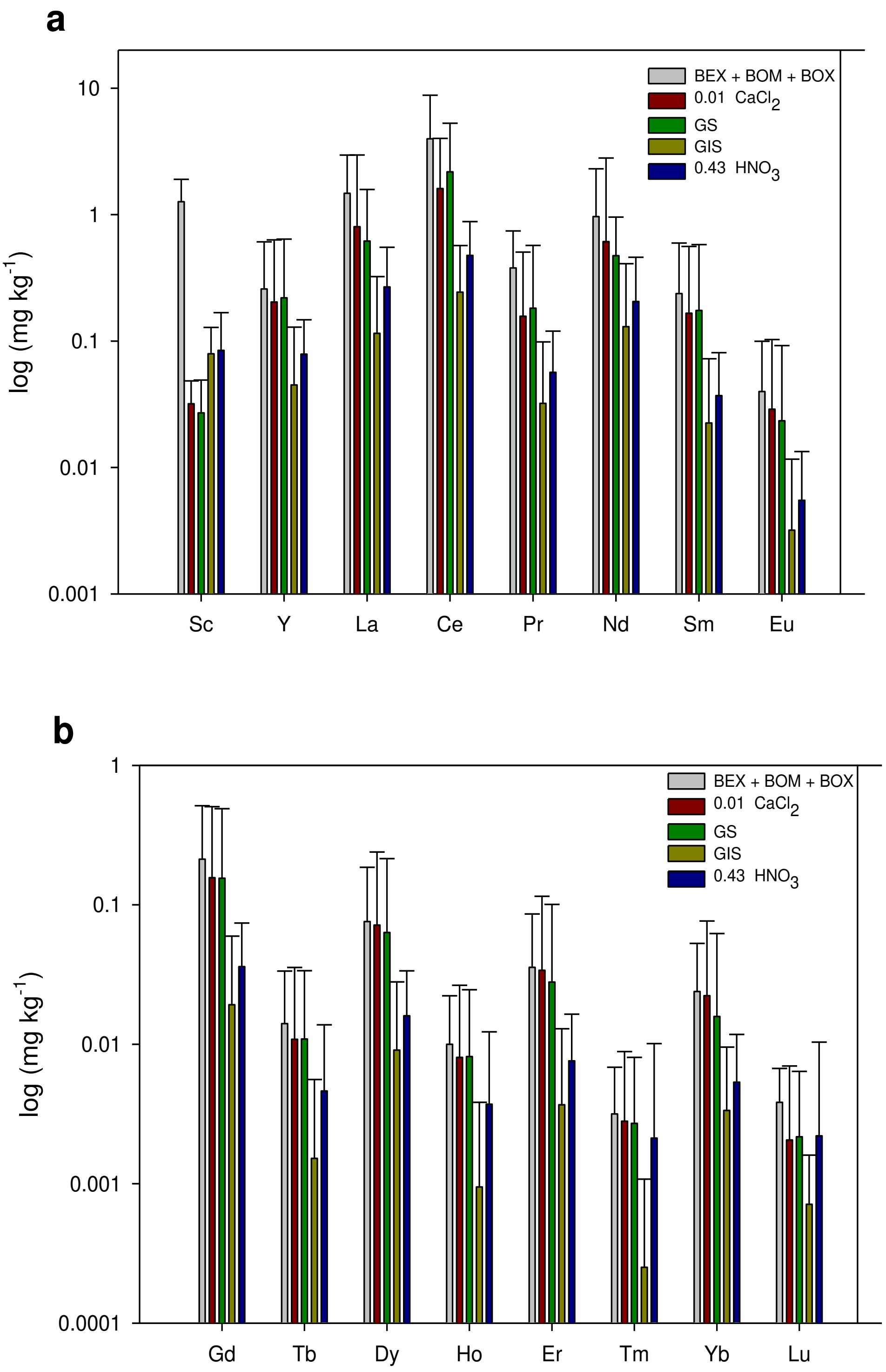


Figure 6: Comparison between the sum of three labile steps of sequential extraction and REE concentration in soils extracted with 0.43 mol L^{-1} HNO_3, 0.01 mol L^{-1} $CaCl_2$, bioaccessibility based on gastric solution (GS) and bioaccessibility based on gastric-intestinal solution (GIS).

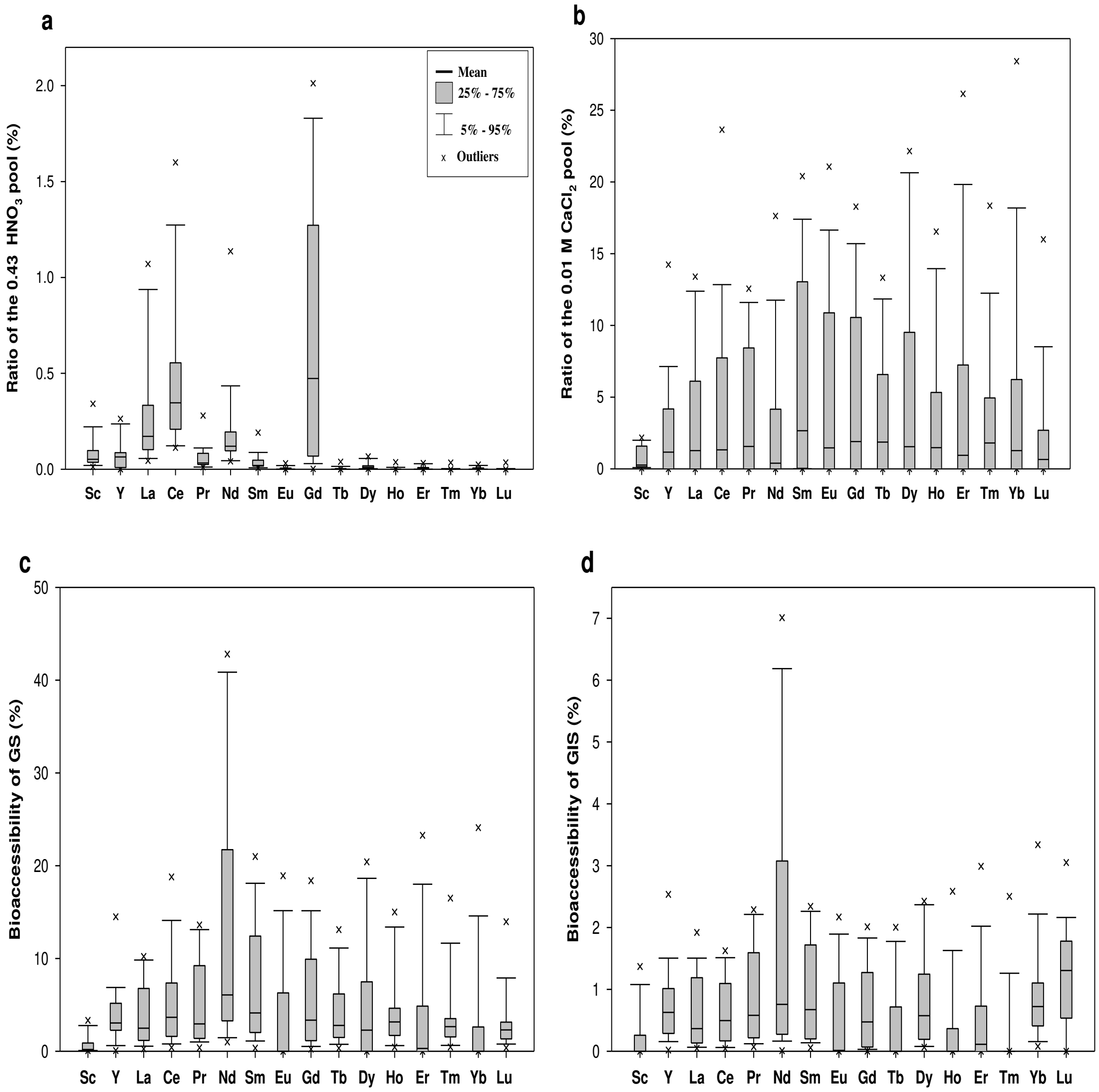


Figure 7: Percentage of REEs concentration extracted with 0.43 mol L^{-1} HNO_3 (a), 0.01 mol L^{-1} $CaCl_2$ (b), bioaccessibility based on gastric solution (GS) (c) and bioaccessibility based on gastric-intestinal solution (GIS) (d).

Table 2: Regression models representing GS concentrations as function of 0.43 HNO_3 and 0.01 mol L^{-1} $CaCl_2$ extractable concentrations.

Element	Equation	r^2
Y	GS = 0.87 (0.01 mol L^{-1} $CaCl_2$) + 0.04	**0.78**
La	GS = 0.42 (0.01 mol L^{-1} $CaCl_2$) + 0.28	**0.89**
Pr	GS = 5.37(0.43 mol L-1 HNO_3) - 0.12	**0.78**
	GS = 1.11(0.01 mol L^{-1} $CaCl_2$) + 0.005	**0.99**
Sm	GS = 7.89(0.43 mol L^{-1} HNO_3) – 0.12	**0.73***
	GS = 1.03(0.01 mol L^{-1} $CaCl_2$) + 0.004	**0.99**
Eu	GS = 6.90(0.43 mol L^{-1} HNO_3) - 0.01	**0.62***
	GS = 0.93(0.01 mol L^{-1} $CaCl_2$) - 0.003	**0.99**
Gd	GS = 6.86(0.43 mol L^{-1} HNO_3) - 0.09	**0.61***
	GS = 0.96(0.01 mol L^{-1} $CaCl_2$) + 0.005	**0.99**
Tb	GS = 0.92(0.01 mol L^{-1} $CaCl_2$) + 0.0009	**0.99**
Dy	GS = 0.90(0.01 mol L^{-1} $CaCl_2$) - 0.001	**0.99**
Ho	GS = 0.89(0.01 mol L^{-1} $CaCl_2$) + 0.001	**0.99**
Er	GS = 0.89(0.01 mol L^{-1} $CaCl_2$) - 0.002	**0.99**
Tm	GS = 0.88(0.01 mol L^{-1} $CaCl_2$) + 0.0003	**0.99**
Yb	GS = 0.85(0.01 mol L^{-1} $CaCl_2$) - 0.003	**0.99**
Lu	GS = 0.85(0.01 mol L^{-1} $CaCl_2$) + 0.0004	**0.99**

All coefficients are significant at the $p < 0.01$ level, with the exception of those indicated by an asterisk which are significant at the $p < 0.05$ level. n=20.

Table 3: Regression models representing GIS concentrations as function of 0.43 HNO_3 and 0.01 mol L^{-1} $CaCl_2$ extractable concentrations**.**

Element	**Equation**	**r^2**
Y	GIS = 0.17(0.01 mol L^{-1} $CaCl_2$) + 0.01	**0.76**
La	GIS = 0.09(0.01 mol L^{-1} $CaCl_2$) + 0.04	**0.93**
Pr	GIS = 0.92(0.43 mol L^{-1} HNO_3) - 0.02	**0.76**
	GIS = 0.19(0.01 mol L^{-1} $CaCl_2$) + 0.001	**0.99**
Nd	GIS = 1.02(0.43 mol L^{-1} HNO_3) - 0.08	**0.86**
	GIS = 0.12(0.01 mol L^{-1} $CaCl_2$) + 0.05	**0.93**
Sm	GIS = 0.98(0.43 mol L^{-1} HNO_3) - 0.01	**0.74**
	GIS = 0.13(0.01 mol L^{-1} $CaCl_2$) + 0.002	**0.99**
Eu	GIS = 0.84(0.43 mol L^{-1} HNO_3) - 0.0014	**0.61***
	GIS = 0.11(0.01 mol L^{-1} $CaCl_2$) – 0.0001	**0.99**
Gd	GIS = 0.84(0.43 mol L^{-1} HNO_3) - 0.01	**0.62***
	GIS = 0.12(0.01 mol L^{-1} $CaCl_2$) + 0.001	**0.99**
Tb	GIS = 0.16(0.01 mol L^{-1} $CaCl_2$) - 0.0003	**0.99**
Dy	GIS = 0.11(0.01 mol L^{-1} $CaCl_2$) + 0.001	**0.99**
Ho	GIS = 0.15(0.01 mol L^{-1} $CaCl_2$) - 0.0003	**0.98**
Er	GIS = 0.11(0.01 mol L^{-1} $CaCl_2$) - 0.0002	**0.99**
Tm	GIS = 0.12(0.01 mol L^{-1} $CaCl_2$) - 0.0001	**0.88**
Yb	GIS = 0.11(0.01 mol L^{-1} $CaCl_2$) + 0.0008	**0.99**
Lu	GIS = 0.17(0.01 mol L^{-1} $CaCl_2$) + 0.0003	**0.88**

All coefficients are significant at the $p < 0.01$ level, with the exception of those indicated by an asterisk which are significant at the $p < 0.05$ level. n=20.

RISK ASSESSMENT

The REE concentration obtained through 0.43 mol L^{-1} HNO_3, 0.01 mol L^{-1} $CaCl_2$, GS and GIS were used to assess the human exposure by oral intake. The risk assessment, as shown by their Hazardous Quotient, of the two population groups (adults and children) are presented in Table 4. Based on the *HQ* results the non-carcinogenic risk was considered low for all REE in all extractors utilized.

The $HQ_{children}$ results based on 0.43 mol L^{-1} HNO_3 presented mean values ranging from $2x10^{-6}$ (Tm, Lu) to $4x10^{-4}$ (Ce), whilst the HQ_{adults} mean values ranged from $1x10^{-7}$ (Tm) to $3x10^{-5}$ (Ce). The $HQ_{children}$ of 0.01 mol L^{-1} $CaCl_2$ ranged from $2x10^{-6}$ (Lu) to $1x10^{-3}$ (Ce) and the HQ_{adults} mean values ranged from $1x10^{-7}$ (Lu) to $1x10^{-4}$ (Ce).

Similarly, the Ce was the element that presented the highest values of *HQ* and Lu present the lowest *HQ* values in both results based on GS and GIS concentration. The $HQ_{children}$ of Ce obtained both in GS, GIS extraction presented mean values of $2x10^{-3}$, and the mean value of HQ_{adults} of Ce was $1x10^{-4}$. While, the $HQ_{children}$ of Lu obtained both in GS and GIS extraction presented mean values of $2x10^{-6}$ and the mean value of HQ_{adults} was $1x10^{-7}$. The REE carcinogenic risk results are presented in Figure 8. The REE carcinogenic risk was regarded as low for all elements analyzed. Similar to non-carcinogenic risk pattern, Ce showed highest carcinogenic risk levels and the lowest risks were observed to Tm and Lu (Figure 8b). Cerium mean carcinogenic values were $4.8x10^{-12}$ for 0.43 mol L^{-1}ol L^{-1} HNO_3, $1.6x10^{-11}$ for 0.01 mol L^{-1} $CaCl_2$, 2.2 $x10^{-11}$ for both GS and GIS.

DISCUSSION

SOIL PROPERTIES

The high acidity and the low bases concentrations observed in the samples soils are common features of Amazon soils due to the strong weathering process and the humid

Table 4: The hazard quotient (*HQ*) for REE obtained in the topsoils samples (0-20 cm) from Amazonas soils

Extractor	Group	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
										HQ							
0.43 mol L^{-1} HNO$_3$	Children	8E-05	7E-05	2E-04	4E-04	5E-05	2E-04	3E-05	5E-06	3E-05	4E-06	1E-05	3E-06	7E-06	2E-06	5E-06	2E-06
	Adults	6E-06	5E-06	2E-05	3E-05	4E-06	1E-05	3E-06	4E-07	2E-06	3E-07	1E-06	3E-07	5E-07	1E-07	4E-07	2E-07
0.01 mol L^{-1} CaCl^{2}	Children	3E-05	2E-04	7E-04	1E-03	1E-04	6E-04	2E-04	3E-05	1E-04	1E-05	7E-05	7E-06	3E-05	2E-06	2E-05	2E-06
	Adults	2E-06	1E-05	5E-05	1E-04	1E-05	4E-05	1E-05	2E-06	1E-05	7E-07	5E-06	5E-07	2E-06	2E-07	2E-06	1E-07
GS	Children	2E-05	2E-04	6E-04	2E-03	2E-04	4E-04	2E-04	2E-05	1E-04	1E-05	6E-05	7E-06	3E-05	2E-06	1E-05	2E-06
	Adults	2E-06	2E-05	4E-05	1E-04	1E-05	3E-05	1E-05	2E-06	1E-05	7E-07	4E-06	6E-07	2E-06	2E-07	1E-06	1E-07
GIS	Children	2E-05	2E-04	6E-04	2E-03	2E-04	4E-04	2E-04	2E-05	1E-04	1E-05	6E-05	7E-06	3E-05	2E-06	1E-05	2E-06
	Adults	2E-06	2E-05	4E-05	1E-04	1E-05	3E-05	1E-05	2E-06	1E-05	7E-07	4E-06	6E-07	2E-06	2E-07	1E-06	1E-07

climate conditions, which favors the leaching of bases (Mafra et al., 2002; Lima et al., 2006; Horbe et al., 2007). The Amazon soils have been under strong wet tropical climate over at least 45 millions of years resulting in the destruction of primary minerals and removal of silica necessary for generation or preservation of 2:1 secondary minerals, which explains the chemical poverty of these soils (Dubroeucq e Volkoff, 1998).

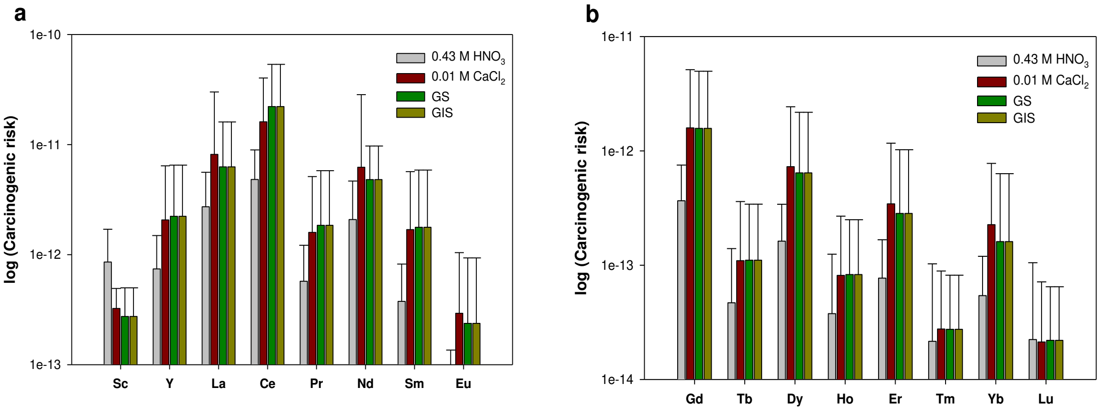


Figure 8: Carcinogenic risk of REE based on single extraction using 0.43 mol L^{-1} HNO_3, 0.01 mol L^{-1} $CaCl_2$, bioaccessibility based on gastric solution (GS) and bioaccessibility based on gastric-intestinal solution (GIS).

REE GEOCHEMICAL MOBILITY

The REE mobility results reflected the chemical and physical characteristics of our soils. Bound to Organic Matter (BOM) was the fraction that presented the lowest REE concentration in this study due to the low levels of TOC in these soils. It may explain the lack of correlation in Spearman analysis obtained in this study between BOM-TOC. The organic matter has an important key role in the REE solubility control, forming stable complex and avoiding leaching losses (Tyler, 2004; Khan et al., 2017a). However, several studies have shown that magnitude of organic matter effects may change due to the chemical and physical soils characteristics (Laveuf et al., 2008; Migaszewski e Gałuszka, 2015). Soils with predominance of sand particles normally presents low concentration of TOC and consequently, minor influence of organic matter pool in the elements geochemical pattern (Laveuf et al., 2008; Yost e Hartemink, 2019).

The BEX concentrations in the soils were below 10% of the **Σ**Fraction, which suggest the low mobility of REE and, consequently the low availability for plant-uptake (Šmuc et al., 2012). Elements in the exchangeable fraction are very labile and normally represent a small portion of total element concentration in soils without intense anthropic activity (Filgueiras et al., 2002). The BEX fraction represents the REE species that are weakly bound to soil particle and may be released easily by ion exchange process (Šmuc et al., 2012; Mihajlovic et al., 2014). Elements bound to exchangeable fraction normally are influenced by adsorption-desorption reactions (Filgueiras et al., 2002).

Our statistical analyses suggested that BEX concentration in the soils are influenced mainly by soil acidity, SB, TOC concentration and Fe_{Ox} (Figure 8). The negative correlation between pH and BEX concentration is explained by the control of soil acidity under the REE adsorption-desorption reactions. In soils with high acidity, the REE tend to be adsorbed in the form of external-sphere complexes on the surface of minerals, while in soils with higher pH values the REE form internal-sphere complexes at the minerals surface (Laveuf et al., 2008). The REE adsorption ratios increase in high pH values due to the release of pH-dependent charges at the mineral surfaces (Brioschi et al., 2013; Migaszewski e Gałuszka, 2015).

The BEX concentrations in Amazon soils are negatively influenced by SB concentration due to the competition between REE and Bases (K^+, Mg^{2+} and Ca^{2+}) in mineral adsorption sites. The predominance of the K^+, Mg^{2+} and Ca^{2+} in the exchange complex favor the shift of REE on their position in mineral surface releasing the REE to soil solution, which may increase the leaching losses. The exchangeable fraction is a dynamic pool and is strongly influenced by the adsorption–desorption reactions, since the natural and unnatural changes in ionic composition may have a strong influence in the REE bound to this soil pool (Šmuc et al., 2012).

The negative correlation observed between BEX-TOC and BEX-Fe_{Ox} are explained by the formation of stable organic complexes of REE and by the incorporation of REE in low crystallinity oxides, facilitated by isomorphic substitution (Laveuf et al., 2008). Both processes decrease the availability of REE and, consequently decrease the REE amount bound to the exchangeable fraction.

Similarly, BOX concentrations are also influenced negatively by pH reactions, which highlight that the pH-dependent charges of the oxides are extremely important for the REE adsorption in these soils. The sorption of REE in the oxides varies with pH and the type of adsorbent, occurring preferably as surface precipitation in the case of Mn oxides and in the surface of Ti and Fe oxides (Ramos et al., 2016; Balaram, 2019). However, the desorption process of REE bound to pH-dependent charges in oxides surface is extremely slow and may be considered not fully available to plants (Šmuc et al., 2012; Brioschi et al., 2013; Migaszewski e Gałuszka, 2015). This hypothesis is reinforced by several literature reports, which indicate the adsorption of REE on hydroxyl-hydrated sites of oxides are very strong (Laveuf et al., 2008; Laveuf e Cornu, 2009).

The remaining phosphorus in solution (P_{Rem}) (Alvarez et al., 2000) is a proxy of the soils ion specific adsorption capacity, and it was inversed correlated significantly to SUM BOX, SUM BEX and, to a lesser extent, to SUM BOM and SUM RES. The relationship with SUM BOX is in line with the reasoning of the predominance of pH dependent charged surfaces, such as kaolinite and Fe and Al oxides, in the clay fraction of these Amazon soils.

The REE incorporated in oxides mineral structure during the geneses process through isomorphic substitution seems to be of minor importance in Amazon soils due to the depletion pattern of HREE. The LREE have larger ion radius than the HREE, which makes it hard for the former to be incorporated in the mineral structures, while the latter are more easily incorporated in the oxides (Laveuf e Cornu, 2009; Mihajlovic et al., 2014).

The RES fraction was influenced negatively by the sand concentration due to the inability of pseudo-total digestion in dissolve the elements embedded in the lattice of silicates

(USEPA, 1998; Mihajlovic et al., 2014). However, the positive correlation between RES and silt concentration suggest the important contribution of primary minerals as REE source in these Amazon soils.

Despite that, the elements associated to residual fraction normally are fixed in the lattices of minerals and are less available to ecosystem pools and only could be released as a result of weathering of long-term (Hu et al., 2006; Šmuc et al., 2012).

REE SINGLE EXTRACTION

The single extractions have been reported as a powerful tool to understand the potential of bioavailable and the bioaccessible fractions of chemical elements mainly due to the low cost and facility to perform (Rao et al., 2010; Rodrigues et al., 2010b). In order to provide a better indication of the effectiveness of single extraction, we compare two potential single extractions, 0.43 mol L^{-1} HNO_3 (Römkens et al., 2009) and 0.01 mol L^{-1} $CaCl_2$ (Houba et al., 2000), with two standard *in vitro* extractions (GS and GIS). The four extractors assessed in this study showed different extraction powers and consequently, the REE concentration obtained in each extraction were different.

The extraction with 0.43 mol L^{-1} showed the lower concentrations in comparison to the other extractions and no correlation between REE-0.43 mol L^{-1} HNO_3 and soil parameters were observed. The use of diluted acid as extractor in studies involving chemical elements in soils have shown satisfactory results mainly due to the stronger acidity ($pH < 1$), which is able to mobilize a large fraction of elements bound to organic matter, amorphous metal oxides and clays surface through pH-control sorption-precipitation-dissolution process (Rao et al., 2010; Rodrigues et al., 2010b, 2018). However, our findings did not exhibit a high effectiveness of REE-0.43 mol L^{-1} HNO_3 extractions in comparison to the sum of the three labile phases and the total concentration. Additionally, the regression match between GS-0.43 mol L^{-1} HNO_3 and

GIS-0.43 mol L^{-1} HNO_3 were only significate for five of REE assessed in our study. Probably, the limited effect of 0.43 mol L^{-1} HNO_3 - extraction could be explained by the low labile concentration of REE (<15%) in these Amazon soil samples and the short time extraction of 0.43 mol L^{-1} HNO_3, which was only two hour, which may influenced the acidity extraction. Several studies have reported that the time of extraction has high influence of the diluted acidity extraction results (Sutherland, 2002; Larner et al., 2006). Possibly, a diluted acid extraction using a extraction-time more than two hours could improve the extraction results (Sutherland, 2002).

On other hand, the 0.01 mol L^{-1} $CaCl_2$ extraction was more effective and showed correlation with soil properties similar to correlation patterns of two standard *in vitro* extractions (GS and GIS). The similarity between 0.01 mol L^{-1} $CaCl_2$ extraction and the standard extractions were also observed in the regression studies, which presented close match for 14 REE in the both GS and GIS prediction. The satisfactory mol L^{-1} $CaCl_2$ extraction results may be explained due to the competitive interaction between the Ca^{2+} and the REE in both inorganic and organic surfaces (Marang et al., 2008; Gonzalez et al., 2014). The surplus of calcium ions in the solution remove the REE ions from mineral surfaces and releasing these elements to solution (Mittermüller et al., 2016).

However, the use of calcium chloride solution for obtaining the bioavailable concentration have presented both satisfactory (Houba et al., 1990, 1996; Lu et al., 2003) and unsatisfactory results (Rao et al., 2010; Rodrigues et al., 2010a) in previous studies involving REE, major elements and trace elements. This pattern suggests that the effectiveness of 0.01 mol L^{-1} $CaCl_2$ could vary with soil chemical and mineralogical characteristics (Liu e Byrne, 1997; Marang et al., 2008). Our data suggest that 0.01 mol L^{-1} $CaCl_2$ is highly effective to remove the REE of their position of surface minerals in soils with high acidity and low sum of bases such as the soils used in this study. On other hand, in soils with high sum of bases, high pH values and significant presence of $CaCO_3$, the use 0.01 mol L^{-1} $CaCl_2$ extraction could not be able to remove the REE of their position, since in these soils no REE-desorption is expected due to the lack of competition between Ca^{2+} and REE^{3+} (Marang et al., 2008; Mittermüller et al., 2016).

The standard extractions (GS and GIS) exhibited divergent results, where the GS extraction presenting REE concentrations higher than REE concentrations as compared to the GIS extraction. The differences between the gastric and the gastric-intestinal bioaccessibility tests have been reported in several studies involving REE and other potentially toxic trace elements, such as Pb, Cd, As and Sb (Oomen et al., 2002; Li et al., 2014a; Wang et al., 2017c; Yan et al., 2020). This discrepancy was attributed to the pH variation of the solutions that simulated human gastro-intestinal fluids, which influences mainly the pH-dependent elements (Wang et al., 2017c). The acid condition (pH=1.5) during the gastric phase increases the solubilization of REE and the lack of complexation with the gastric components explain the high REE concentration in this phase (Wang et al., 2017c; Yan et al., 2020). On the other hand, during the transition to the intestinal phase the pH increase to 7.0 causes the REE precipitation and also re-adsorption on soil particles (Yan et al., 2020). Additionally, some studies have reported that components of the gastrointestinal solution may chelate the cations and cause their precipitation (Li et al., 2014a; Wang et al., 2017b), which may decrease the concentration of REE in the intestinal solution.

Despite of this discrepancy, the use of both GS extraction and GIS and others *in vitro* methods are strongly recommended to environmental studies because they can be used to analyze large numbers of soil samples and provide a more reliable estimate of the bioavailable pool than total concentrations in contaminated soils (Boros et al., 2017; Yan et al., 2020). Several authors have reported that only the gastric phase results can provide a conservative and low cost approach for estimating the oral bioaccessibility (Li et al., 2014a; Boros et al., 2017).

The gastric-intestinal essays reflect the *in vivo* bioavailability more accurately than gastric-only extraction methods, due to complete simulation of the gastric-intestinal process of humans (Oomen et al., 2002; Mingot et al., 2011). However, gastric-intestinal essays normally are expensive and long time-consuming analytical protocol (Mingot et al., 2011).

HEALTH RISK ASSESSMENT

The non-carcinogenic assess results obtained through 0.01 mol L^{-1} $CaCl_2$, GS and GIS extraction showed similar results due to the characteristics of these extractors as discussed in the previous topic. All HQ results obtained in our study were inferior to 1 in both children and adults group, which denote the low possibility of non-carcinogenic risk by REE exposure according to the general non-carcinogenic risk classification (USEPA, 2004).

However, data about REE assessment through HQ are scarce and there is no regional screening levels guides. Previous studies involved in REE assessment in contaminated areas have shown that the HQ results are higher than 1.8×10^{-2} for children and higher than 3×10^{-3} for adults (Sun et al., 2017; Guo et al., 2019), which are values considerably higher than those one observed in our study. The elevated sensibility of non-carcinogenic risk in children group observed in our study seems to be a general pattern in studies involved risk assessment by potentially toxic elements (Guo et al., 2019; Ferreira et al., 2021b). Children normally are more sensitive to contamination by ingestion pathway due to the hand-mouth activity. Besides that, children could exhibit more potential health risks due to their low body weight and uncomplete formation of physiologic system (Rodríguez-Barranco et al., 2014; Sun et al., 2017). Based on HQ results from China cities, values of HQ higher than 0.1 for children are a indicative for government's attention (Sun et al., 2017).

Similarly to non-carcinogenic risk, our carcinogenic assessment associated to REE exposure were considered low ($<1\times10^{-6}$) (Faiz et al., 2012; Sun et al., 2017). The absence of

REE contamination risks observed in this study are in line with the previous REE results for Amazon soils. Ferreira et al. (2021a), observed that the ecological risk by REE contamination were considered low in Amazon soils, although these authors observed the existence of slight unnatural enrichment in the REE concentrations. Studies in plants of Amazon showed the REE concentration in plant tissue were high in areas when the REE concentration in soils were high (Cunha et al., 2012), which may suggests the existence of a certain mobility of REE in the food chain in the Amazon ecosystem. The expressive mobility of REE in the food chain of some ecosystem have been reported in the literature and regular monitoring in these areas are strongly recommended to avoid animal and human contaminations in the future (Meryem et al., 2016; Squadrone et al., 2019).

CONCLUSIONS

The sequential extraction procedure showed that the REE concentrations in Amazon topsoils are mainly associated to the residual phase and the bioavailable fractions (exchangeable phase, organic matter phase and Fe/Mn oxides phase) represent less than 20% of the total amount of REE in these soils. Similarly, the oral bioaccessibility obtained through two *in vitro* methods and two single-step extractions represent less than 20% of the total amount for the majority of the REE analyzed.

Statistical analyses suggested the REE concentrations of the bioavailable fractions and in the oral bioaccessibility, concentrations are influenced by soil properties such as soil acidity, base saturation, organic carbon concentration, specific ion adsorption and mineralogical forms of Fe oxides, all of them in inverse relationship.

The oral bioaccessibility estimated by single-step extraction with 0.01 mol L^{-1} $CaCl_2$ present promisor results and yielded similar results for 14 REE as compared to the commonly applied *in vitro* methods to determine the oral bioaccessible fraction. Due to the low cost and the easy analytical protocol, the extraction with mol L^{-1} $CaCl_2$ has a great potential to be adopted as standard method in REE contamination monitoring programs in Amazon soils especially in residential areas due to the more accuracy to assess human bioaccessibility concentrations compared to total and pseudo-total digestion methods.

The non-carcinogenic risk and the carcinogenic risk associated to the oral exposure by REE was considerably low for both children and adults in all the soil samples. Due to the scarcity of REE bioaccessibility data in Brazilian soils, our data may serve as a basis for defining initial guideline values for non-carcinogenic risk and the carcinogenic risk associated to oral exposure of REE.

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APPENDIX 2

Table S1: Rates of addition-recovery experiments analyses of geochemical speciation.

Samples	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Exchangeable fraction																
S8 +10 µg/kg	103%	101%	101%	108%	100%	103%	97%	92%	96%	94%	96%	94%	94%	94%	95%	95%
S8 +30 µg/kg	95%	98%	101%	104%	95%	99%	97%	95%	96%	101%	93%	99%	93%	98%	87%	98%
S8 +50 µg/kg	101%	90%	93%	93%	98%	92%	91%	91%	92%	98%	100%	97%	87%	96%	105%	98%
Bound to organic matter phase																
S8 +10 µg/kg	85%	101%	102%	103%	101%	102%	97%	98%	99%	99%	99%	99%	98%	98%	99%	98%
S8 +30 µg/kg	86%	107%	98%	100%	98%	97%	95%	98%	99%	98%	98%	97%	96%	96%	99%	100%
S8 +50 µg/kg	86%	104%	100%	102%	96%	94%	96%	98%	97%	101%	103%	98%	94%	98%	103%	99%
Bound to Fe/Mn oxides phase																
S8 +10 µg/kg	95%	99%	88%	109%	103%	107%	104%	96%	97%	107%	102%	102%	101%	100%	99%	96%
S8 +30 µg/kg	93%	93%	105%	104%	107%	105%	108%	107%	108%	103%	98%	98%	98%	95%	95%	94%
S8 +50 µg/kg	94%	96%	97%	102%	103%	106%	106%	101%	99%	105%	101%	102%	97%	98%	96%	95%
Residual fraction																
S8 +10 µg/kg	100%	102%	101%	100%	100%	95%	101%	99%	96%	103%	97%	100%	102%	102%	100%	101%
S8 +30 µg/kg	98%	101%	100%	98%	98%	100%	98%	103%	99%	101%	98%	101%	104%	101%	103%	101%
S8 +50 µg/kg	95%	101%	104%	99%	99%	107%	104%	102%	99%	106%	102%	96%	102%	100%	102%	100%

Table S2: Rates of addition-recovery experiments analyses of bioaccessibility fraction.

Samples	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Single extraction with 0.43 mol L^{-1} HNO_3																
S8 +10 µg/kg	100%	90%	107%	107%	106%	107%	106%	105%	107%	106%	108%	107%	106%	107%	106%	106%
S8 +30 µg/kg	103%	110%	111%	110%	109%	110%	107%	106%	105%	106%	107%	107%	106%	106%	107%	107%
S8 +50 µg/kg	98%	108%	108%	108%	107%	108%	104%	104%	104%	103%	104%	105%	103%	103%	104%	104%
Single extraction with 0.01 mol L^{-1} $CaCl_2$																
S8 +10 µg/kg	103%	106%	96%	96%	98%	103%	97%	103%	109%	98%	97%	98%	92%	98%	103%	96%
S8 +30 µg/kg	104%	106%	98%	98%	98%	103%	99%	96%	111%	98%	96%	97%	90%	98%	108%	97%
S8 +50 µg/kg	105%	110%	100%	100%	99%	103%	102%	102%	103%	99%	98%	98%	98%	97%	97%	97%
Gastric solution concentration (GS)																
S8 +10 µg/kg	99%	109%	97%	95%	97%	101%	97%	96%	97%	96%	94%	96%	94%	94%	93%	95%
S8 +30 µg/kg	98%	109%	97%	95%	97%	100%	96%	96%	97%	96%	95%	95%	95%	94%	94%	95%
S8 +50 µg/kg	89%	108%	93%	91%	96%	100%	94%	93%	94%	94%	94%	95%	93%	94%	92%	95%
Gastric-intestinal solution concentration (GIS)																
S8 +10 µg/kg	86%	109%	109%	113%	108%	112%	108%	106%	108%	107%	108%	107%	108%	109%	111%	112%
S8 +30 µg/kg	84%	111%	99%	101%	98%	99%	97%	97%	98%	98%	98%	96%	94%	94%	95%	96%
S8 +50 µg/kg	85%	110%	104%	107%	103%	106%	102%	101%	103%	102%	103%	101%	101%	102%	103%	104%

Table S3: Limit of detection (LD) for REEs determination procedure by ICP-MS

	Sc	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Exchangeable fraction																
LD (µg L^{-1})	0.145	0.001	0.006	0.020	0.002	0.010	0.001	0.001	0.002	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Bound to organic matter phase																
LD (µg L^{-1})	0.134	0.002	0.012	0.011	0.000	0.008	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Bound to Fe/Mn oxides phase																
LD (µg L^{-1})	0.054	0.028	0.339	0.687	0.059	0.176	0.022	0.005	0.026	0.001	0.005	0.001	0.003	0.001	0.002	0.002
Residual fraction																
LD (µg L^{-1})	0.057	0.004	0.019	0.030	0.005	0.009	0.045	0.023	0.034	0.004	0.045	0.012	0.071	0.008	0.054	0.024
Single extraction with 0.43 mol L^{-1} HNO_3																
LD (µg L^{-1})	0.001	0.203	0.096	0.290	0.001	0.075	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Single extraction with 0.01 mol L^{-1} $CaCl_2$																
LD (µg L^{-1})	0.06	0.020	0.201	0.450	0.030	0.14	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Gastric solution concentration (GS)																
LD (µg L^{-1})	0.052	0.013	0.309	0.683	0.042	0.211	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Gastric-intestinal solution concentration (GIS)																
LD (µg L^{-1})	0.237	0.018	0.103	0.205	0.022	0.068	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.002

LD: (3 x Blank Standard Deviation)/ Linear Regression Slop

Table S4: Parameters used to calculate for REEs exposure and human health risk

Parameter	**Symbol**	**Value**	**Units**	**Reference**
Element concentration	C	-	mg kg^{-1}	-
Body weight Adult	Bw (a)	70	kg	IBGE (2010)
Body weight Children	Bw (c)	15	kg	IBGE (2010)
Averaging time Adult	At (a)	9125	day	USEPA (2007)
Averaging time Children	At (c)	2190	day	USEPA (2007)
Exposure frequency	EF	250	day $year^{-1}$	USEPA (2007)
Exposure duration Adult	ED (a)	25	year	USEPA (2007)
Exposure duration Children	ED (c)	6	year	USEPA (2007)
Ingestion rate Adult	IR (a)	100	mg day^{-1}	USEPA (2007)
Ingestion rate Children	IR (c)	200	mg day^{-1}	USEPA (2007)
Contact rate Adult	Cr (a)	100	mg day^{-1}	USEPA (2007)
Contact rate Children	Cr (c)	200	mg day^{-1}	USEPA (2007)
Corresponding reference dose	RfD	0.02	mg $(kg \times day)^{-1}$	Sun et al. (2017)

Table S5: Chemical parameters of topsoils samples (0-20 Cm) from Amazonas soils.

Samples	**pH$_{KCl}$**	**pH$_w$**	**SB**	**CEC$_e$**	**TOC**	**P$_{Rem}$**	**CEC$_{pH7}$**	**Sand**	**Silt**	**Clay**	**Fe$_{OX}$**	**Fe$_{DCB}$**
			cmol$_c$/dm^{-3}	cmol$_c$/dm^{-3}	%	mg/L	cmol$_c$/dm^{-3}	------------%------------			------g/kg-----	
S1	3.95	4.94	0.18	2.94	0.08	14.10	4.58	46.20	18.70	35.00	0.64	63.17
S2	3.81	4.77	0.21	4.94	0.08	12.10	8.01	23.80	30.00	46.30	0.38	23.66
S3	3.87	5.21	0.13	2.30	0.08	20.60	3.73	58.40	16.40	25.20	0.66	77.43
S4	4.10	5.02	1.04	2.03	0.00	35.50	2.84	83.10	5.90	11.00	0.73	92.45
S5	4.48	5.30	16.66	3.69	0.90	39.20	7.29	74.70	0.90	24.40	7.91	29.01
S6	5.43	5.43	19.18	4.22	0.82	33.40	4.92	63.30	0.50	36.20	5.43	34.62
S7	4.38	5.19	10.92	2.94	0.82	38.70	4.94	45.10	5.10	49.80	7.61	36.30
S8	3.91	4.63	17.82	2.96	0.30	50.00	6.96	63.00	1.30	35.70	4.17	28.13
S9	4.69	5.55	18.17	3.21	0.90	39.50	4.91	82.60	0.70	16.70	5.95	26.37
S10	5.73	6.79	23.64	3.69	0.15	21.90	4.19	72.00	5.80	22.20	8.42	70.91
S11	3.12	3.70	16.28	2.82	0.30	23.00	7.72	45.60	9.20	45.20	7.78	27.29
S12	4.50	5.33	6.22	3.23	0.90	40.60	3.53	17.90	1.70	80.40	2.63	7.88
S13	4.27	4.89	0.37	0.96	1.01	20.40	3.47	36.00	9.70	54.40	4.66	108.78
S14	3.85	4.84	0.20	4.63	0.08	13.30	6.5	53.70	13.40	32.90	1.27	73.55
S15	3.90	4.91	0.22	4.46	0.00	15.10	5.62	52.60	11.30	36.10	7.35	41.82
S16	3.86	4.85	0.26	5.97	0.08	11.80	7.56	36.80	19.30	43.90	0.76	37.07
S17	3.92	4.90	0.19	4.33	0.23	10.30	5.59	39.40	15.80	44.80	0.55	36.09
S18	3.90	4.77	0.17	5.19	0.16	4.40	6.87	34.40	22.40	43.30	1.31	109.27
S19	3.97	4.94	0.10	3.25	0.00	10.90	4.7	42.60	48.50	8.90	0.91	105.84
S20	3.92	4.42	0.23	3.88	0.31	7.10	6.23	36.10	8.90	55.00	3.83	92.57
Maximum	5.73	6.79	23.64	5.97	1.01	50.0	8.01	83.10	48.50	80.40	8.42	109.27
Mean	4.18	5.02	6.61	3.58	0.36	23.1	5.51	50.37	12.28	37.37	3.65	56.11
Median	3.94	4.93	0.32	3.47	0.19	20.5	5.27	45.90	9.45	36.15	3.23	39.44
Minimum	3.12	3.70	0.10	0.96	0.00	4.4	2.84	17.90	0.50	8.90	0.38	7.88
Standard Deviation	0.58	0.58	8.59	1.17	0.37	13.5	1.57	18.40	11.80	16.85	3.01	32.59

GENERAL CONCLUSION

The geochemical pattern of REEs present a large variation in Amazonas soils. The soils of Solimões basin present high concentrations of REEs due to the influence of alluvial and fluvial Andean deposition. Whereas, the soils of Rio Negro basin present low concentrations of REEs due to the leaching losses and the sandy texture associated of parent material characteristics. The geochemical mobility analysis showed that the REE concentrations in Amazon topsoils are mainly associated to the residual phase and the bioavailable fractions. Whilst, the REEs associated to oral bioaccessibility represent less than 20% of the total concentrations. The use of single-step extraction with 0.01 mol L^{-1} $CaCl_2$ was promisor for estimate the concentration associated to oral bioaccessibility in compare traditional *in vitro* methods. The soil contamination risk and the health risk associated to REEs exposure were considered low to both children and adults.