GUILHERME SOARES DINALI

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Thesis submitted for the degree of Doctor in Soil Science with the Departamento de Ciência do Solo, Universidade Federal de Lavras, Brazil.

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RESUMO GERAL

Os terras raras (ETR) são um grupo de 17 elementos cada vez mais presentes na indústria, agricultura e vida cotidiana do mundo atual. Os minérios fosfatados são conhecidos por conter ETR em concentrações variáveis. Esses fosfatos são matérias-primas de fertilizantes fosfatados constantemente aplicados nos solos, especialmente em agroecossistemas tropicais. Os teores de ETR presentes nas matérias primas de produtos fosfatados bem como as mudanças de fases cristalinas associadas ao processamento realizados na indústria de fertilizantes fosfatados são praticamente desconhecidos. Em geral os solos são considerados importantes fontes, desses e de outros elementos, devido aos seus teores naturais ou a adição constante de fertilizantes. Todavia, poucas pesquisas têm sido conduzidas no intuito de verificar os teores de ETR nos solos e insumos agrícolas bem como o comportamento desses elementos nos agroecossistemas. Assim, para entender melhor o conteúdo dos ETR em fertilizantes fosfatados – que são as principais fontes difusas de ETR para o meio ambiente -, bem como a adsorção de ETR em solos de textura e mineralogia diferentes, o presente estudo teve como objetivo: i) avaliar ETR em concentrados de fosfato utilizados como matérias-primas na indústria de fosfato na América do Sul, bem como em produtos finais - incluindo fertilizantes fosfatados, fosfato di-cálcio e fosfogesso-, a fim de caracterizar seus teores de ETR, assinaturas e fases cristalinas portadoras de ETR; e ii) avaliar o comportamento de adsorção de todos os ETR em solos sob diferentes condições experimentais, a fim de modelar e prever a adsorção e o destino do ETR nos solos. Em relação aos produtos de fosfato, nossos resultados mostraram que o conteúdo de ETR em matérias-primas e produtos da indústria de fosfato na América do Sul é altamente variável. Considerando os materiais de origem ígnea, o concentrado de fosfato do Complexo Mineroquímico de Catalão apresentou o maior teor total de ETR (ΣETR de até 16.650 mg kg^{-1}) e as maiores concentrações de ETR leves (ΣLETR / ΣETR ~ 98%). Uma grande variedade de fases minerais foi encontrada não apenas nos concentrados de fosfato, mas também em produtos finais, com o grupo das apatitas que apareceram como principal fase cristalina portadora de ETR. Os conteúdos e composição de ETR nos produtos finais foram fortemente influenciados pelas respectivas matérias-primas, resultando em uma forte combinação das assinaturas de ETR, o que reforça a utilidade das assinaturas como ferramentas precisas para rastrear a origem e a proveniência dos produtos finais da indústria fosfatada de fertilizantes. Com relação aos experimentos de adsorção, diferentes ETR foram adsorvidos em quantidades semelhantes nos pH's naturais do solo. A adsorção dos ETR aumentou com o aumento do pH, especialmente no solo tropical. Cério é o ETR adsorvido em quantidades mais elevadas enquanto o lutécio foi o menos adsorvido, independentemente do solo estudado. O modelo de Langmuir foi usado eficientemente para ajustar os dados de adsorção e estimar a capacidade máxima de adsorção (ETR$_{CMA}$) e a força de adsorção (KL), exceto para os solos tropicais arenosos. A capacidade tampão de ETR (ETR$_{CT}$) demonstrou ser um ótimo parâmetro para entender o comportamento do ETR nos solos. Considerando a importância cada vez maior dos ETR como contaminantes emergentes, esse trabalho quantificou e qualificou ETR em fertilizantes e ainda demonstrou dados relevantes para prever o comportamento de ETR nos agroecossistemas, bem como o destino e o transporte desses elementos em solos de mineralogia e textura contrastantes.

Palavras-chave: Elementos Terras Raras. Contaminantes emergentes. Mineralogia de minerais. Solos tropicais. Adsorção

GENERAL ABSTRACT

Rare earth elements (REY) are a group of 17 elements of an ever-growing presence in present-day industries, agriculture, and in everyday life. Phosphate ores are well-known for containing REY in a wide range of contents. Such phosphates are raw materials of many fertilizers that have been constantly applied to soils, especially in Tropical agroecosystems. Because of that, the environmental concentrations of REY are expected to increase accordingly. Our current understanding of the role of different P products as carriers of REY to soils is still incipient, especially regarding the extent to which the original REY content in raw materials remains in their respective products and the changes in crystalline phases associated with the phosphate ore processing. Furthermore, while soils have been considered important sinks for such elements through addition of fertilizers and other sources of REY, yet little research has been conducted concerning REY contents, inputs, and behavior in such ecosystems. Thus, to better understand REY contents in P fertilizers - a major diffuse source of REY to environment -, as well as REY sorption on soils of different genesis - a major sink of REY -, the present study aimed to: i) evaluate REY in phosphate concentrates used as raw materials in major phosphate industries in South America as well as in final products – including P fertilizers, di-calcium phosphate, and phosphogypsum –, in order to characterize their REY contents, signatures, and REY-carrying crystalline phases; and ii) evaluate the adsorption behavior of all REY in soils under different experimental conditions in order to model and predict sorption and fate of REY in soils. Regarding phosphate products, our results showed that the REY content in raw materials and products from the phosphate industry in South America is highly variable. Considering materials of igneous origin, the phosphate concentrate from the Catalão Minerochemical Complex presented the highest total REY content ($\sum$REY up to 16,650 mg kg^{-1}) and the highest concentrations of light REY ($\sum$LREY/$\sum$REY ~98%). A great variety of mineral phases were found not only in phosphate concentrates but also in final products, with the apatite-group appearing as the main REY-carrying crystalline phase. The REY contents and composition in the final products were generally strongly influenced by their respective raw materials, resulting in a strong match of REY signatures, which reinforces the usefulness of REY signatures as accurate tools for tracing the origin and provenance of final products of the P fertilizer industry. With respect to sorption experiments, the different REY were sorbed in similar amounts at the natural soils pH's. REY sorption increased with increasing pH, especially in a tropical soil. Cerium is the REY sorbed in higher amounts whereas lutetium is the lowest sorbed REY, irrespectively of the studied soil. The Langmuir model was efficiently used to fit adsorption data and to estimate maximum adsorption capacity (REY$_{MAC}$) and sorption strength (KL), except for sandy tropical soils. The REY buffering capacity (REY$_{MBC}$) has demonstrated to be a great parameter to understand REY behavior on soils. Considering the ever-increasing importance of REY as emerging contaminants, our findings are relevant to predict REY behavior in agroecosystems, as well as REY fate and transport in soils of contrasting mineralogy.

Keywords: Rare earth elements. Emerging contaminants. Ore mineralogy. Tropical soil. Sorption.

FIRST PART

1 GENERAL INTRODUCTION

Rare earth elements (REY) are seventeen chemical elements with atomic numbers ranging from 57, lanthanum (La) to 71, Lutetium (Lu). Yttrium (Y) and scandium (Sc), with atomic numbers 39 and 21 respectively, are also included in this group. Commonly, the scientific community divide REY in two distinct groups: the light ones - LREY (Lanthanum - La, Cerium - Ce, Praseodymium - Pr, Neodymium - Nd, Promethium - Pm, Samarium - Sm and, Europium - Eu), and the heavy ones - HREY (Dysprosium - Dy, Holmium - Hm, Erbium - Er, Thulium - Tm, Ytterbium - Yb, Lutecium - Lu and, Yttrium - Y) (Šmuc et al., 2012). Scandium is usually not included in either the LREY or the HREY classification (Gupta and Krishnamurthy, 1992). This distinction is based on their physical-chemical features and their ionic radius. The similarity in ionic radius makes REY interchangeable in most minerals. As a result, obtaining pure REY is very difficult and costly (Gupta and Krishnamurthy, 2005).

REY have wide application in the worldwide industry due to their unique chemical, magnetic, and luminescent properties. These applications have grown intensely in the last three decades. This is mainly due to the great advance in electronic devices, such as smartphones and tablets. Furthermore, REY have been used in the manufacture of crystal liquid, monitors and televisions displays, optic fiber cables that provide much greater bandwidth than copper wires, polished glasses, mirrors, precision lenses, magnets, electrical and electronic components of several audio devices and video, military communication systems, among others (Crow, 2011; Meyer and Bras, 2011; Preinfalk, C., Morteani, 1986).

Despite the great industrial knowledge about REY uses, the environment role of them is still unclear. Even so, REY have been released in the environment in many ways. Anthropogenic actions, such as phosphate fertilizer application and improper electronic material disposal have been pointed as the main causes of REY addition to the environment (Aubert et al., 2002; Hu et al., 2006; Laveuf and Cornu, 2009; Smidt, 2011; Zhang and Shan, 2001). Ramos et al. (2016) have mentioned several sources of REY to the environment, yet

these authors have pointed that phosphate fertilizers employed in agriculture are the main diffuse sources of REY to soils, even unintentionally. Also, REY input in the environment happens through disposal of many different materials uses in the everyday life (El-Ramady, 2010).

Rare earth elements have been associated with a variety of minerals including silicates, oxides, carbonates, phosphates, and halides (Levy, 1924; Vijayan et al., 1989). Among all minerals, phosphates are the ones that contribute the most to REY supply to the soil. Taunton et al. (2000) and Tyler (2004) report that phosphate minerals may contain high concentrations of REY, stating that these concentrations are directly related to mineral genesis (Picard et al., 2002). Volokh et al. (1990) and Redling (2006) pointed out that long-term phosphate fertilizers are large suppliers of soil REY. In Brazil, Turra et al. (2011) have concluded that the levels of REY in phosphate fertilizers are very variable. In fact, REY concentrations in phosphate fertilizer depend directly of the raw material (Ramos et al., 2016a). In the last decades, many studies have used REY as tracers (Alderton et al., 1980; Alibo and Nozaki, 1999; Dołęgowska and Migaszewski, 2013; Ilyin, 1998; Laveuf et al., 2008; Ling et al., 2013; Nance and Taylor, 1976; Sciences, 2008; Sha and Chappell, 1999; Trail et al., 2012; Wang et al., 2011; Yang et al., 2012). Considering that REY are the main elements that respect the "Oddo-Harkins" rule, REY signatures are interesting tools for a better understanding of different environmental process and to track possible environmental contaminations. Nevertheless, concerning the role of REY, there is no common sense in the scientific community if REY are essential for life or toxic for the environment (Tyler, 2004).

The current trend of increasing use of phosphate fertilizers in agroecosystemns, especially in Tropical regions, speaks for the need of additional studies evaluating not only the levels of REY in fertilizers, but also their behavior in soils. It is widely known that soil properties and soil solution composition affect sorption on soils (Alloway, 1990). REY adsorption in soils is influenced by clay type and content, and, to a higher extent, also by the presence of aluminum silicates and iron and manganese oxides (Pang et al., 2002). Several studies have addressed the magnitude and mechanisms of REY sorption in soil. Jones (1997) have reported that the adsorption of La, Y, Pr, and, Gd is pH-depended. Pang et al. (2002) have described that REY sorption capacity in soils is clay- and oxides-type dependent, with the last ones having higher REY sorption capacity. On the other hand, Bao and Zhao (2008) have demonstrated that the aluminosilicates (i.e., kaolinite and smectite) also have a great

ability to sorb REY. Piasecki and Sverjensky (2008) have mentioned that lanthanide sorption on the surface of clays occurs in the form of "clay-REY", that is, the species are subject to cation exchange, and that reactions are reversible at the clay exchange sites, i.e., the adsorption of REY on the soil particles occurs through the formation of outer sphere complexes. Luo and Byrne (2004) have shown that hydroxides and carbonates are the main inorganic binders / complexants of REY. Caspari et al. (2006) studied the occurrence of REY in the soil and found that light REY are mainly associated with clayey soils, while heavy REY are more associated with soils with coarser materials, such as sandy ones. Regarding the REY sorption on the organic matrix of the soil, the REY behavior is very similarly to that of other trace elements. Pourret et al. (2007) and Tang and Johannesson (2010) have concluded in their studies that the stability constants for REY bounded with humic substances vary according to the molar ratio between REY and dissolved organic carbon. These authors have observed that the concentrations of REY are inversely correlated with the pH of the soil, but directly correlated with the concentrations of dissolved organic carbon.

Although important, most of these experiments were conducted under specific conditions, i.e. specific organo-mineral phases, specific pH, or with only one REY. These studies may not represent the real REY adsorption in natural soils, as soil is a complex and heterogeneous system, with many constituents into its mineral and organic phases. In face of the soil complexity, it is important to perform REY adsorption experiments not only using specific solid phases, but also using the entire soil sample, and involving all REY, as they are found in the environment. Moreover, it is well known the ability of REY to remain always together in specific molar ratios, regardless of the chemical environment. Thus, the study of the behavior of REY in soil must be carried out as they are found in the environment (fertilizers, soils, source materials), i.e., all together.

In face of this, this work sought to investigate: i) what are the REY levels that might be introduced in the environment through phosphate fertilizers; and, ii) how REY are adsorbed in soils of distinct physical, chemical, and mineralogical features and under different experimental conditions. For that, REY contents, REY signatures, and REY-carrying crystalline phases in phosphate concentrates used as raw materials in key phosphate industries in South America, as well as in selected final products were analyzed. Later, REY sorption was evaluated on contrasting soils from USA and Brazil. Adsorption experiments were carried out in a wide pH range, using different REY concentrations and in individual as well as

competitive systems. It is expected that this investigation will help us better understand the role of products of the P fertilizer industry as carriers of REY to soils and the food chain. In addition, it will allow us to advance the knowledge regarding qualitative and quantitative information about REY in raw materials and final products of the P fertilizer industry in South America, as well as to trace the origin of phosphate fertilizers with the use of REY signature. Moreover, the information provided will assist us to better understand REY sorptive behavior in natural soils, while offering also useful information for environmental regulations and/or for plant nutrition studies, since the role of REY in the environment is still a matter of research.

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SECOND PART – PAPERS

PAPER 1

Rare earth elements in raw materials and products of the phosphate fertilizer industry in South America: content, signature, and crystalline phases

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ABSTRACT

Phosphate ores are well-known for containing rare earth elements (REE) in a wide range of contents. The presence of REE in phosphate (P) products may enhance plant and animal development. Yet, our current understanding of the role of different P products as carriers of REE to soils is still incipient, especially regarding the extent to which the original REE content in raw materials remains in their respective products and the changes in crystalline phases associated with the phosphate ore processing. This study evaluated phosphate concentrates used as raw materials in major phosphate industries in South America as well as final products – including P fertilizers, di-calcium phosphate, and phosphogypsum –, in order to characterize their REE contents, signatures, and REE-carrying crystalline phases. The results showed that the REE content in raw materials and products from the phosphate industry in South America is highly variable. Phosphorites from Bayóvar Phosphate Mine showed the lowest REE content among the studied raw materials (~70 mg kg^{-1}). Considering materials of igneous origin, the phosphate concentrate from the Catalão Minerochemical Complex presented the highest total REE content ($\sum$REE up to 16,650 mg kg^{-1}) and the highest concentrations of light REE ($\sum$LREE/$\sum$REE ~98%), whereas those from the Araxá Minerochemical Complex, especially materials from the F4 Mine, presented the highest contents of heavy REE ($\sum$HREE ~1,200 mg kg^{-1}). A great variety of mineral phases was found not only in phosphate concentrates but also in final products, with the apatite-group appearing as the main REE-carrying crystalline phase. The REE contents and composition in the final products were generally strongly influenced by their respective raw materials, resulting in a strong match of REE signatures, which reinforces the usefulness of REE signatures as accurate tools for tracing the origin and provenance of final products of the P fertilizer industry.

Keywords: REE, apatite, carbonatite, phosphorite, ore mineralogy, REE signature

1. Introduction

Rare earth elements (REE) are a group of seventeen chemical elements comprising yttrium (Y), scandium (Sc) and the 15 lanthanide elements (lanthanum-La, cerium-Ce, praseodymium-Pr, neodymium-Nd, promethium-Pm, samarium-Sm, europium-Eu, gadolinium-Gd, terbium-Tb, dysprosium-Dy, holmium-Ho, erbium-Er, thulium-Tm, ytterbium-Yb, and lutetium-Lu). These elements have similar properties and, consequently, are usually found together in geologic deposits of phosphate rock.

In Brazil, over 90% of the mined phosphate ores come from igneous complex carbonatite deposits, accounting for 2% of the estimated worldwide reserves (Zhang et al., 2012). Although there is almost no large-scale exploitation of rare earth minerals in Brazil, the existing resources are significant and occur mainly in association with alkali-carbonatitic complexes (Antoniassi et al., 2015). The main process involved in the genesis of this kind of complex is the residual concentration

of unweathered or slightly weathered ore minerals (e.g., apatite) due to the dissolution of carbonates. In these deposits there are several REE-bearing minerals, usually present at extremely fine grain (Cavalcante et al., 2014; Neumann and Medeiros, 2015). As reported by Ani and Sarapaa (2013) carbonatite rocks are known to contain the highest amounts of REE among all igneous rocks, but where these elements reside among the variety of mineral species found in carbonatite is less well understood.

Phosphate ores are well-known for having a wide range of REE contents, and indirect application of REE to agricultural soils is widespread due to their presence in many products of the phosphate fertilizer industry (Otero et al., 2005; Turra et al., 2011; Waheed et al., 2011). Several studies have shown positive effects of REE in plants and animals (Cai et al., 2015; He et al., 2010; Hu et al., 2004; Ma et al., 2014). However, our knowledge of the biological role of REE is still in its early stages (Skovran and Martinez-Gomez, 2015). Hypotheses supporting the beneficial effects of REE in plant and animal metabolism include stimulation of the antioxidant system, increased absorption and utilization of nutrients, increased electron transport rate in the photochemical phase of photosynthesis, and reduction of intestinal pathogens growth (de Oliveira et al., 2015; Giraldo et al., 2014; He et al., 2010; Ramos et al., 2016).

The most common process used in the production of phosphate fertilizers is the rock phosphate attack with concentrated sulphuric acid and water. In this process the main products from chemical reactions are phosphoric acid (H_3PO_4), single superphosphate (SSP), triple superphosphate (TSP), and the hydrated calcium sulphate (phosphogypsum), which is one of the by-products of phosphate rock processing. In spite of the widespread use of many products of the P fertilizer industry in agriculture, the current understanding of the role of different P products as carriers of REE to soils is still incipient, especially regarding the extent to which the original REE content in raw materials remains in their respective products and the changes in crystalline phases associated with the phosphate ore processing.

This study evaluated REE contents, REE signatures, and REE-carrying crystalline phases in phosphate concentrates utilized as raw materials in key phosphate industries in South America, as well as in selected final products. Information provided by this investigation will help us better understand the role of products of the P fertilizer industry as carriers of REE to soils and the food chain. In addition, it will allow us to advance the knowledge regarding qualitative and quantitative information about REE in raw materials and final products of the P fertilizer industry in South America, as well as to trace the origin of phosphate fertilizers with the use of REE signatures.

2. Material and methods

Different materials from major producing areas of phosphate industry in Brazil and Peru were sampled, including 12 processed raw materials and 8 products. All materials were sampled twice, in 2013 and 2014, in triplicate. The sampled materials and their respective sites are listed in Table 1. The manufacturing process flowsheet is similar to all phosphate concentrate, and comprises crushing, grinding, desliming, flotation, leaching, filtration, drying, and packaging. The rock phosphate from Bayovar is an exception to that, because it is only grinded.

For analyses of REE, the solid samples were air-dried and ground to pass through a 150-mesh nylon sieve. All solid samples were digested by means of an alkaline fusion method. In brief, an aliquot of 0.1 g from each sample was fused with 1.4 g of lithium metaborate in platinum crucibles at 1000°C in a fusion machine (Fluxer BIS, Claisse, Québec, Canada). After cooling, the resulting bead was dissolved in beakers containing 50 mL of a 2.5% solution of tartaric acid and 10% HNO_3. Each beaker was then transferred to a hot plate at 120 ± 20°C with magnetic stirring for complete solubilization. After that, the samples were transferred to 100-mL polypropylene volumetric flasks and the volume was completed with a 2.5% solution of tartaric acid and 10% HNO_3. For phosphoric acid (samples in liquid form), a 1000-fold diluted solution was directly analyzed for REE content.

A certified reference material (Calcareous Soil ERM-CC690®, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium) was included for quality control. Blank and certified reference samples were added to the analytical series. The REE contents in the digested solutions were determined by inductively coupled plasma-mass spectrometry (ICP-MS, Model NexION 300D, Perkin Elmer, Waltham, MA, USA). Typical instrumental settings used during this study are summarized in Table 2.

For clustering the samples based on their REE signatures, the REE contents for each sample were first transformed by dividing them by the respective Ce content in the sample in order to remove the influence of total REE content on the REE signature. Based on the transformed REE contents, a matrix of Euclidean distances among samples was calculated and used for hierarchical clustering using the Ward's algorithm (Ward, 1963). The bootstrap support for each branch in the resulting dendrogram was calculated using the pvclust package (Suzuki and Shimodaira, 2006).

The crystalline structures of solid samples were evaluated by X-ray diffraction using a synchrotron light source (LNLS, Campinas, Brazil). In short, the samples were air-dried and ground to pass through a 50-mesh nylon sieve. Then, the samples were inserted in capillary quartz samplers with 0.3-mm inner diameter and 0.001-mm thickness. The degree-2θ goniometry of Debye–Scherrer was chosen for data acquisition and analysis. The incident beam was monochromatic, obtained by a DCM-double crystal monochromator, with Si (111). The measurements were made with a wavelength λ = 1.04021 nm, 2θ in the 5–120° range, and 2.0 s/step. The resulting diffractograms were interpreted with

the aid of the mineralienatlas and webminerals databases (mineralienatlas.com, 2016; webmineral.com, 2016) using in-house R scripts (Team, 2015).

3. Results

The mean REE concentrations of the standard reference materials obtained by ICP-MS and their respective mean recoveries are presented in Table 3. They show the reliable analytical data accuracy for REE provided by this method.

The REE contents in phosphate concentrate and products varied widely (Fig. 1), with higher levels being found in samples from igneous origin – e.g., from Catalão, Araxá, and Tapira in Brazil – and lower contents in the sample of sedimentary origin, i.e., the Bayóvar phosphorite from Peru. In general, the highest levels of light rare earth elements (LREE - La, Ce, Pr, Nd, and Sm) and ∑REE were found in samples from Catalão, while the highest levels of heavy rare earth elements (HREE - Gd, Tb, Dy, Ho, Er, Tm, Yb, and Y) were observed in samples from Araxá (Fig. 2). The accumulation order of LREE in all samples in descending order was Ce > La > Nd > Pr > Sm > Eu. However, Nd content was higher than that of La in some samples from Araxá and Cajati. For HREE, the accumulation order was Y > Gd > Dy > Er > Tb > Yb > Ho > Tm, whereas Y showed lower concentration than Gd in all raw materials from Catalão.

Table 4 shows the annual production and the estimated exportation of REE for the materials with the highest levels of these elements. We observed that annual REE flow in the Catalão Complex for conventional and ultrafine phosphate concentrates, and SSP are currently 13, 2.5, and 2.1 thousand tons per year, respectively. For the Tapira Phosphate Mine, the current major source of phosphate concentrate in Brazil, the estimated output for LREE, HREE and ∑REE are about 13, 0.8, and 14 thousand tons, respectively. For the Uberaba Industrial Complex, about 1.6 million tons of phosphogypsum are produced per year, resulting in an estimated annual flow of about 8 thousand tons of REE.

Ultrafine phosphate concentrates, which are concentrated in the clay-sized fraction, showed higher REE content than conventional phosphate concentrates for all sampling sites. By comparing the total REE levels between phosphate concentrates and their respective products, we observed that about 50-60% of the initial concentration of these elements in the raw material remains in the superphosphates. For the dicalcium phosphate, which is widely used as a dietary supplement in animals, about 20% of the original REE content remains in the product. Finally, for phosphoric acid and its derived product, MAP, the remaining REE level can vary from less than 5% in the former to about 29% in the latter. Therefore, single superphosphate (SSP) from Catalão and Araxá, and triple superphosphate and phosphogypsium from Uberaba are relevant sources of REE for agricultural soils, with high concentrations of Ce, La, and Nd, generally much more abundant than other REE.

To assess whether the products can be traced back to their respective raw materials based on REE signature, we performed a hierarquical clustering analysis on the matrix of euclidean distances calculated from REE levels normalized by the Ce concentration in each sample. The results are presented in the form of a dendrogram in Fig. 3, which shows seven clearly distinct clusters, two of them (VI and VII) having only one sample and five others (I-V) having 2-4 samples consistently grouped, with a bootstrap support higher than 80%. Cluster I was predominately composed of materials from the Barreiro Mine in Araxá and the SSP from Araxá. Cluster II includes raw materials and SSP from the Catalão Minerochemical Complex, having very homogeneous REE signatures and grouping with a bootstrap support of 100%. Group III, with a bootstrap support of 97%, includes both conventional and ultrafine phosphate concentrates from the Tapira Phosphate Mine, as well as TSP and phosphogypsum from Uberaba Industrial Complex. In fact, phosphate concentrates from Tapira are fed to the Uberaba Industrial Complex by a mineral pipeline for the production of TSP, phosphoric acid, and phosphogypsum (a by-product). The Araxá Minerochemical Complex has two operational mines, F4 Mine and Barreiro Mine, whose phosphate concentrates are normally used for SSP production. The grouping of SSP from Araxá with samples from the Barreiro Mine (Group I), rather than with those from F4 Mine (Group V), indicates that this SSP was produced with raw materials from the Barreiro Mine. This grouping was probably due to their lower proportion of HREE when compared with raw materials from F4 Mine. Finally, Group IV was composed by raw materials from Cajati, whereas the raw material from Patos the Minas and the dicalcium phosphate from Cajati were completely distinct from all other samples with regards to their REE signatures, each forming separate groups.

We found a great diversity in terms of mineral phases in phosphate concentrates and also in the final products, with apatite, carbonate-fluorapatite, and carbonate-hydroxyapatite being the major crystalline components carrying REE in the samples analyzed, with a minor presence of accessory mineral phases, e.g. anatase, britholite, rutile, loparite, and tritomite (Fig. 4). In general, Brazilian phosphate concentrates, especially from Catalão, Araxá, and Tapira, contained a more diverse array of REE-carrying mineral phases than the sedimentary phosphorite from Bayóvar-Peru.

4. Discussion

In Brazil, the raw materials used to produce phosphate fertilizers are mostly igneous, metasedimentary, carbonatitic, and lateritic from the Precambrian age. These deposits are made up of different minerals, among which apatite is the most abundant, with enrichment of REE in some locations, especially in those with rocks of carbonatitic origin (Lapido-Loureiro et al., 1989). Hughes et al. (1991) reported that among all igneous rocks, those containing carbonatitic apatite have the highest REE contents, which renders this mineral the most important one in controlling REE content in

igneous rocks. Fleischer and Altschuler (1986) who published an analysis of REE in apatite from many origins, observed that igneous apatite shows a diverse REE composition, usually containing high LREE content. On the other hand, in sedimentary apatite they found very low levels of LREE, with higher levels of yttrium (Y) in some locations. In agreement with these studies, we observed that phosphorite from Peru showed extremely low REE levels, with Y being the most abundant REE. Piper et al. (1988) also reported low levels of REE in phosphorite from the Peru shelf, with Y predominating over all other REE for some samples. In contrast, the Brazilian phosphate concentrates analyzed in our study, especially those from Catalão, showed considerable amounts of REE, for instance, the total REE content (∑REE) for ultrafine concentrate, conventional concentrate, and SSP from Catalão were 16,649; 15,333 and 8,365 mg kg^{-1}, respectively, about twice as much as those levels found in materials from Araxá and Cajati. Catalão is one of the biggest phosphate mines in Brazil, and is described as a lateritic rare earths deposit related to hydrothermal and supergene origin in dolomitic carbonatite rocks, presenting important apatite, Ba-pyrochlore, anatase, and REE mineralizations (Tassinari et al., 2001). According to these authors, the REE deposit in Catalão is located in the south border of the open pit of the phosphate mine, having a substantial overlay with it. Our results indicates that Catalão phosphate mine is enriched in REE relative to most other phosphate ores that have been studied to date (Emsbo et al., 2015).

In the wet process for phosphoric acid manufacturing, when the phosphate concentrate is dissolved with sulfuric acid and recycled as diluted phosphoric acid, about 70-80% of the initial REE in the concentrate is retained in the leaching residue of phosphogypsum, with only 20-30% being dissolved in the phosphoric acid leaching solution (Preston et al., 1996; Zhang et al., 2012). In the present study, the phosphogypsum, TSP, MAP, and phosphoric acid from Uberaba are manufactured mainly with phosphate concentrate from Tapira, which is fed into the Uberaba Industrial Complex by a mineral pipeline 125 km long, the first in the world built for this purpose. We found that approximately 70% of ∑REE initially present in the raw materials from Tapira remained in the phosphogypsum produced in the Uberaba Industrial Complex (about 70% for LREE and 50% for HREE). For phosphoric acid, these values were lower, less than 15% for LREE and about 20% for HREE.

The current advances in flotation technology are allowing complex low-grade phosphorus deposits to be exploited economically. The continuous reduction in grade is forcing industries to produce ultrafine particles in order to liberate P-containing particles from the ore. It is standard practice in the Brazilian phosphate industry to separate the ultrafine concentrates by scrubbing and hydrocycloning. In the present study, we found higher REE contents in ultrafine concentrates than in conventional concentrates, especially for LREE. For instance, La, Ce, Pr, and Nd contents were 30, 31, 28, and 25% higher, respectively, in the ultrafine than in the conventional phosphate concentrate in the

F4 Mine of Araxá. It is generally assumed that REE are concentrated in the clay-sized fraction; they also concentrate in fine-grained sediments because their host minerals, including accessory primary and secondary minerals, usually occur in that size range (Cavalcante et al., 2014; Singh, 2009). As described by Cullers et al. (1979) the bulk of the REE elements reside in the fine-grained (clay and silt) fraction, regardless of clay mineralogy, and also in trace minerals such as zircon, monazite, and apatite. Neumann and Medeiros (2015) reported that Araxá's phosphate ore, as usual for deeply weathered ores, is very fine-grained. Tassinari et al. (2001) who determined the mineralogical compositions and evaluated the potential for mineral concentration through physical processes for saprolitic ore samples from Catalão, also showed that REE are usually present at extremely fine grain sizes. On the other hand, we found that Tb, Dy, Ho, and Er were higher in conventional than in ultrafine phosphate concentrate in Tapira.

Due to their physicochemical properties, REE have been extensively used as tracers of genesis, origin, and geochemical processes in many studies (Laveuf and Cornu, 2009; Laveuf et al., 2012; Smidt et al., 2011). We found similar REE fingerprints among raw materials and their products, indicating their suitability for tracing the materials utilized for phosphate fertilizers manufacturing. REE provides an excellent tracer because they are on fine particles and are probably not influenced by deposition and other fractionating processes (Olmez and Gordon, 1985). But, in some situations, when the industrial process involves purification steps (e.g. MAP production) and introduction of different mineral material (e.g. dicalcium phosphate production) the REE signature of final products can change, making it difficult to identify their raw material based on their REE signature. However, in general, we observed that REE signatures were preserved along the process of phosphate fertilizers production and, therefore, they can be used to identify the raw materials used for each product.

The Brazilian alkaline igneous rocks have a diversified mineralogical composition, which includes phosphates (e.g., carbonate-, hydroxy-, and fluorapatites), oxides (e.g., magnetite, anatase, and perovskite), semi-soluble salts (e.g., pyrite, calcite, and dolomite), and silicates (e.g., quartz, pyroxenes, and clay minerals) (Marino et al., 2012). In the present study, all phosphate concentrates were beneficiated from phosphate ore by using a combination of comminution, screening, scrubbing, and hydrocyclones in order to remove clays, fine-grained iron-aluminum phosphates, and fine-grained iron oxides. We found that apatite, fluorapatite, and hydroxyapatite, taken together, are the most abundant crystalline phases in raw materials and products, with quartz being the most abundant gangue mineral, especially for raw materials. Neumann and Medeiros (2015) who studied the mineralogical and technological characteristics of the Araxá complex REE (Nb-P) ore, also found that quartz is the main gangue mineral. We also observed a higher diversity of REE-carrying crystalline phases in the superphosphates than in their respective raw materials. This may be due to dissolution-reprecipitation of REE minerals after the sulfuric acid attack on the raw material, and to the residual concentration of

insoluble minerals not detected in the raw materials. The diffraction patterns obtained by conventional XRD usually reveal dominant mineral components, while minor phases are generally at the level of background noise or are unresolved from overlapping dominant reflection. In our study, synchrotron X-ray diffraction was used to give high intensity and high-resolution diffraction data, which provided higher accuracy in identifying mineral phases in all samples analyzed.

Phosphate fertilizers are extensively applied worldwide, and encompass broad REE levels diversity (Abdel-Haleem et al., 2001; Otero et al., 2005; Turra et al., 2011). REE levels in fertilizers are relevant because of the potential loads of REE on the environment associated with fertilizer application. Therefore, the knowledge of REE concentration in fertilizers is essential for assuring food and environmental safety, especially for areas of intensive agriculture. On the other hand, these elements can also have beneficial effects on plant growth, as indicated by several studies worldwide showing increases in seed germination, root growth, chlorophyll content, plant resistance, and agricultural productivity after REE application (d'Aquino et al., 2009; de Oliveira et al., 2015; Hu et al., 2004; Maksimovic et al., 2014; Ramos et al., 2016). In China, fertilizers are enriched with such elements due to their expected positive effects on plants. Such information are still very scarce for Brazilian agriculture.

In our study, we observed that REE contents in phosphate fertilizers reflect the REE levels in phosphate concentrates, both in regard to their content (Fig. 1) and to their signatures (Fig. 3). Cerium was always the dominant REE, followed by La, Nd, Pr, and Sm. Among the products analyzed, the maximum REE concentration was found for single superphosphate (SSP) from Catalão ($\sum$REE = 8,365 mg kg^{-1}), followed by phosphogypsum from Uberaba ($\sum$REE = 5,041 mg kg^{-1}), SSP from Araxá ($\sum$REE = 4,681 mg kg^{-1}), TSP ($\sum$REE = 4,375 mg kg^{-1}), and MAP ($\sum$REE = 2,062 mg kg^{-1}) from Uberaba. This results indicates that considerable amount of REE are been deposited in Brazilian soils, and potential effects of these are still unknown. Di-calcium phosphate is usually produced by reacting calcium carbonate with phosphoric acid. Consequently, the REE found in di-calcium phosphate in our study ($\sum$REE = 354 mg kg^{-1}) are probably coming from the calcium carbonate used in its production because REE could not be detected in the phosphoric acid from Cajati. Di-calcium phosphate is used as a core raw material in food supplements for cattle, poultry, pets, and shrimps. Previous studies have shown that dietary supplementation with REE could enhance animal nutrient utilization, minimize the growth of intestinal pathogens, and may act as cofactors that replace calcium or other metallic ions during various biological processes, including egg formation in laying hens (Cai et al., 2015; He and Rambeck, 2000; He et al., 2010). The favorable scenario for the REE adds value to the present study because the REE-fertilizers may have agronomic effect and di-calcium phosphate with REE could increase the animal performance.

Regarding the demand side, REE are classified as specialty materials rather than commodities, which implies that the need for them is predominantly driven by technological progress. These elements were identified as having high risk of supply shortage and high impact on the economy (Hislop and Hill, 2011). Considering the importance for strategic sectors of the economy with risks of supply shortage, Moss et al. (2013) described the following REE as "critical": dysprosium (Dy), europium (Eu), terbium (Tb), yttrium (Y), praseodymium (Pr), and neodymium (Nd). We observed that Nd, Pr, and Y are present in larger amounts than Dy, Eu, and Tb in the samples studied. The highest levels of Nd and Pr were found in raw materials from the Catalão Minerochemical Complex, while materials from the Araxá Minerochemical Complex had the largest contents of Y, Dr, Eu, and Tb.

The significant outflow of REE, as reported in table 4, could be economically exploited, especially the Catalão mine (Tassinari et al., 2001) which has the larger amount of LREE, and the Araxá mine, which showed higher levels of HREE. Phosphogypsum containing REE represents a potentially valuable resource (Zhang et al., 2012) and REE present in this material from the Uberaba Industrial Complex could be promising to be exploited. Considering the phosphogypsum stacks is estimated to be ~40 million tons, and the mean of $\sum REE$ found in this study (~5,000 mg kg^{-1}), the content of REE could be about 200 thousand tons.

It is important to evaluate phosphate fertilizers as a source of REE for agricultural ecosystems. If we consider that the main Brazilian phosphate fertilizers are SSP, TSP, and MAP, we estimate that the use of these fertilizers adds approximately 10.5 thousand tons of REE to Brazilian soils. Such amount is close to annual consumption of important micronutrients (e.g., boron, copper, manganese, and zinc) in Brazilian agriculture (Ramos et al., 2016).

Finally, as discussed earlier, REE occurring in phosphate products may enhance plant and animal performance, but those effects probably depend on the bioavailability of REE, which for phosphate fertilizers are not yet known. Thus, further studies on REE contents in products from the P fertilizer industry need to focus on the total as well as the bioavailable fraction of REE. The total REE content in phosphate products varied by about three orders of magnitude in this study and this variation may be used in the future as an additional criterion to value phosphate fertilizers.

5. Conclusions

This study showed that the REE content in raw materials and products from phosphate industry in South America are highly variable. The phosphorite from Bayóvar Phosphate Mine has the lowest REE content among the studied raw materials (ΣREE ~70 mg kg^{-1}). Among those raw materials of igneous origin, the phosphate concentrates from the Catalão Minerochemical Complex presented

the highest total REE content (ΣREE up to 16.650 mg kg^{-1}) and the highest concentrations of light REE (ΣLREE/ΣREE ~98%), whereas those from the Araxá Minerochemical Complex, especially the materials from F4 Mine, presented the highest contents of heavy REE (ΣHREE ~1.200 mg kg^{-1}).

A variety of mineral phases in phosphate concentrates and also in products was found, and the apatite-group seems to be the main crystalline phase that carries REE.

The REE contents in the products were generally strongly influenced by their respective raw materials. Consequently, the REE signatures in the final products of the P fertilizer industry in South America allow, in most cases, the accurate identification of their respective raw materials.

Acknowledgments

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List of Tables

Table 1. Raw materials and products collected for this study

Abbreviations	Samples	Characteristic	Sampling site
Ufine P – Cat	Ultrafine phosphate concentrate	Raw material	Catalão minerochemical complex, State of Goiás – Brazil
Conv P – Cat	Conventional phosphate concentrate	Raw material	
SSP – Cat	Single superphosphate	Fertilizer	
Ufine P Bar – Arx	Ultrafine phosphate concentrate from Barreiro mine	Raw material	Araxá minerochemical complex, State of Minas Gerais - Brazil
Conv P Bar – Arx	Conventional phosphate concentrate from Barreiro mine	Raw material	
Ufine P F4 – Arx	Ultrafine phosphate concentrate from F4 mine	Raw material	
Conv P F4 – Arx	Conventional phosphate concentrate from F4 mine	Raw material	
SSP – Arx	Single superphosphate	Fertilizer	
Ufine P – Tap	Ultrafine phosphate concentrate	Raw material	Tapira phosphate mine, State of Minas Gerais - Brazil
Conv P – Tap	Conventional phosphate concentrate	Raw material	
TSP – Ubb	Triple superphosphate	Fertilizer	Uberaba industrial complex, State of Minas Gerais - Brazil
MAP – Ubb	Monoamonium phosphate	Fertilizer	
PhosGyp – Ubb	Phosphogypsum	Fertilizer	
H_3PO_4 – Ubb	Phosphoric acid	Raw material	
Calc P – Caj	Calcitic phosphate concentrate	Raw material	Cajati minerochemical complex, State of São Paulo – Brazil
Dol P – Caj	Dolomitic phosphate concentrate	Raw material	
H_3PO_4 – Caj	Phosphoric acid	Raw material	
$CaHPO_4$ – Caj	Dicalcium phosphate	Animal consumption	
Conv P – PaM	Conventional phosphate concentrate	Raw material	Patos de Minas phosphate mine, State of Minas Gerais - Brazil
P Rock – Bay	Phosphate rock	Raw material/fertilizer	Bayóvar phosphate mine, Piura Region – Peru

Table 2. Typical instrumental settings for REE determination in raw materials and products of the phosphate fertilizer industry used in this study.

Instrument	Perkin Elmer NexIon 300D
RF Power	~ 1300 W
Spray Chamber and Nebulizer	Scott (Ryton) with concentric nebulizer
Coolant argon flow rate	15 min−1
Auxiliary argon flow rate	1.0 min−1
Nebulizer argon flow rate	0.8–1.2 min−1 (adjusted daily to obtain optimum signal intensity and stability)
Sample uptake rate	Approximately 4.00 mL min−1
Sampler cone	Nickel, 1.1 mm aperture i.d.
Skimmer cone	Nickel, 0.9 mm aperture i.d.
Instrument tuning	Performed using a 1 ng g−1 multi-element solution
Ion transmission	N 27.000 cps per 1 ng g−1 indium
Rinse time between standards or samples	60 s (with 1% v/v HNO3)
Take-up and stabilisation time	15 s
Ion sampling depth	Adjusted daily to obtain maximum signal intensity
Ion lens settings	Adjusted daily to obtain maximum signal intensity and optimum resolution

Table 3. Certified value, determined concentration and REE recovery on certified materials.

REE	Certified value[1] (mg kg^{-1})	Obtained value (mg kg^{-1})	Mean recovery (%)
Ce	49.1	48.38 ± 0.45	98.5
Dy	2.9	2.87 ± 0.08	97.6
La	24.4	24.06 ± 0.21	98.6
Nd	19.1	20.0 ± 0.23	104
Yb	1.57	1.54 ± 0.09	98

[1] Certified reference material ERM-CC690-calcareous soil.

Table 4. Annual production and the exported amount of REE for the materials studied.

Site	Material	Annual production (t)a	Estimated exportation (t)b		
			LREE	HREE	∑REE
Catalão minerochemical complex	Ultrafine P concentrate	150,000	2447 (22)	50 (4)	2497 (22)
	Conventional P concentrate	860,000	12,891 (200)	295 (9)	13,186 (200)
	SSP	260,000	2125 (42)	50 (2)	2175 (42)
Araxá minerochemical complex	Ultrafine P concentrate Barreiro Mine	70,000	517 (2)	60 (1)	577 (2)
	Conventional P concentrate Barreiro Mine	130,000	879 (4)	95 (2)	974 (5)
	Ultrafine P concentrate F4 Mine	170,000	1302 (18)	211 (5)	1513 (19)
	Conventional P concentrate F4 Mine	320,000	1884 (36)	341 (13)	2225 (38)
	SSP	650,000	2736 (106)	306 (33)	3043 (111)
Tapira phosphate mine	Ultrafine P concentrate	160,000	1081 (3)	59 (1)	1140 (13)
	Conventional P concentrate	1,860,000	12,077 (301)	724 (19)	12,801 (301)
Uberaba industrial complex	TSP	810,000	3289 (140)	254 (9)	3544 (140)
	MAP	850,000	1554 (47)	199 (20)	1753 (50)
	Phosphogypsum	1,600,000	7784 (311)	283 (16)	8067 (310)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb
Ufine P – Cat	3,800 ±89	7,871 ±74	888 ±76	3,066 ±31	358 ±33	88 ±2	242 ±8	19 ±1	73 ±6	209 ±25	9 ±1	18 ±2	1 ±0.4	7 ±1
Conv P – Cat	3,415 ±135	7,187 ±144	826 ±98	2,886 ±43	354 ±47	87 ±14	235 ±35	18 ±2	76 ±2	213 ±10	9 ±1	19 ±1	1 ±0.3	7 ±2
SSP – Cat	1,926 ±83	3,934 ±65	447 ±66	1,529 ±98	184 ±20	42 ±4	112 ±4	9 ±1	38 ±3	122 ±6	5 ±1	11 ±1	1 ±0.5	5 ±1
Ufine P Bar – Arx	1,513 ±11	3,224 ±20	408 ±7	1,626 ±3	280 ±3	86 ±2	245 ±2	30 ±1	153 ±4	568 ±20	24 ±1	54 ±1	5 ±0.2	29 ±1
Conv P Bar – Arx	1,360 ±18	3,021 ±17	378 ±5	1,480 ±21	247 ±5	72 ±1	203 ±3	24 ±1	116 ±2	511 ±16	18 ±1	41 ±1	4 ±0.3	19 ±1
Ufine P F4 – Arx	1,530 ±18	3,281 ±100	430 ±12	1,710 ±13	315 ±9	100 ±6	290 ±19	39 ±3	208 ±19	826 ±22	34 ±3	80 ±8	9 ±1	47 ±6
Conv P F4 – Arx	1,093 ±89	2,505 ±45	336 ±38	1,370 ±32	256 ±13	82 ±2	246 ±11	38 ±2	183 ±15	694 ±38	31 ±3	71 ±7	8 ±1	41 ±4
SSP – Arx	895 ±68	1,866 ±138	235 ±19	899 ±51	149 ±7	43 ±3	123 ±2	15 ±1	78 ±2	322 ±51	12 ±1	27 ±2	3 ±0.5	14 ±1
Ufine P – Tap	1,680 ±46	2,960 ±51	370 ±8	1,346 ±39	196 ±11	53 ±5	149 ±17	14 ±2	65 ±5	245 ±6	10 ±1	22 ±1	1 ±0.3	12 ±1
Conv P – Tap	1,566 ±92	2,888 ±93	348 ±25	1,301 ±89	190 ±16	52 ±4	148 ±14	17 ±1	83 ±4	238 ±9	12 ±1	27 ±2	1 ±0.3	11 ±1
TSP – Ubb	953 ±72	1,801 ±141	217 ±18	814 ±65	132 ±9	36 ±2	108 ±5	11 ±1	51 ±5	214 ±9	8 ±1	18 ±1	1 ±0.5	11 ±1
MAP – Ubb	399 ±18	809 ±48	96 ±3	373 ±17	68 ±4	20 ±2	63 ±7	5 ±1	33 ±2	168 ±23	5 ±1	13 ±1	1 ±0.3	9 ±1
PhosGyp – Ubb	1,142 ±68	2,204 ±152	267 ±25	984 ±96	138 ±9	35 ±1	95 ±7	10 ±1	38 ±3	108 ±9	5 ±1	11 ±1	0.7 ±0.3	4 ±1
H_3PO_4 – Ubb	66 ±6	109 ±11	13 ±2	61 ±18	21 ±8	8 ±2	6 ±1	4 ±1	27 ±11	6 ±1	5 ±2	16 ±3	0.3 ±0.1	1.5 ±0.1
Calc P – Caj	296 ±8	722 ±18	95 ±3	405 ±3	67 ±1	18 ±1	55 ±2	4 ±1	23 ±1	75 ±2	4 ±1	6 ±1	0.6 ±0.3	3 ±1
Dol P – Caj	294 ±7	731 ±8	98 ±2	417 ±4	74 ±1	23 ±1	61 ±1	5 ±1	28 ±1	82 ±3	4 ±1	8 ±1	0.6 ±0.3	3 ±1
H_3PO_4 – Caj	<4	<7	<1	<1	<2	<2	<4	<0.2	<0.5	<3	<0.2	<1	<0.2	<1
$CaHPO_4$ – Caj	73 ±2	149 ±3	14 ±1	62 ±1	11 ±1	3 ±1	12 ±1	1 ±0.5	5 ±1	24 ±1	<0.2	<1	<0.2	<1
Conv P – PaM	64 ±2	122 ±4	15 ±1	64 ±1	14 ±1	3 ±1	13 ±1	1 ±0.5	11 ±1	96 ±7	1 ±0.5	6 ±1	0.8 ±0.3	4 ±1
P Rock – Bay	15 ±1	<7	<1	<1	<2	<2	<4	1 ±0.5	4 ±1	47 ±1	<0.2	4 ±1	<0.2	<1

Fig. 1.

Heatmap showing means and standard errors ($n = 3$) of REE contents for 20 samples of processed raw materials and products from phosphate fertilizer industry (mg kg^{-1}) (see Table 1 for abbreviations). Within each column, darker colors indicate higher REE contents.

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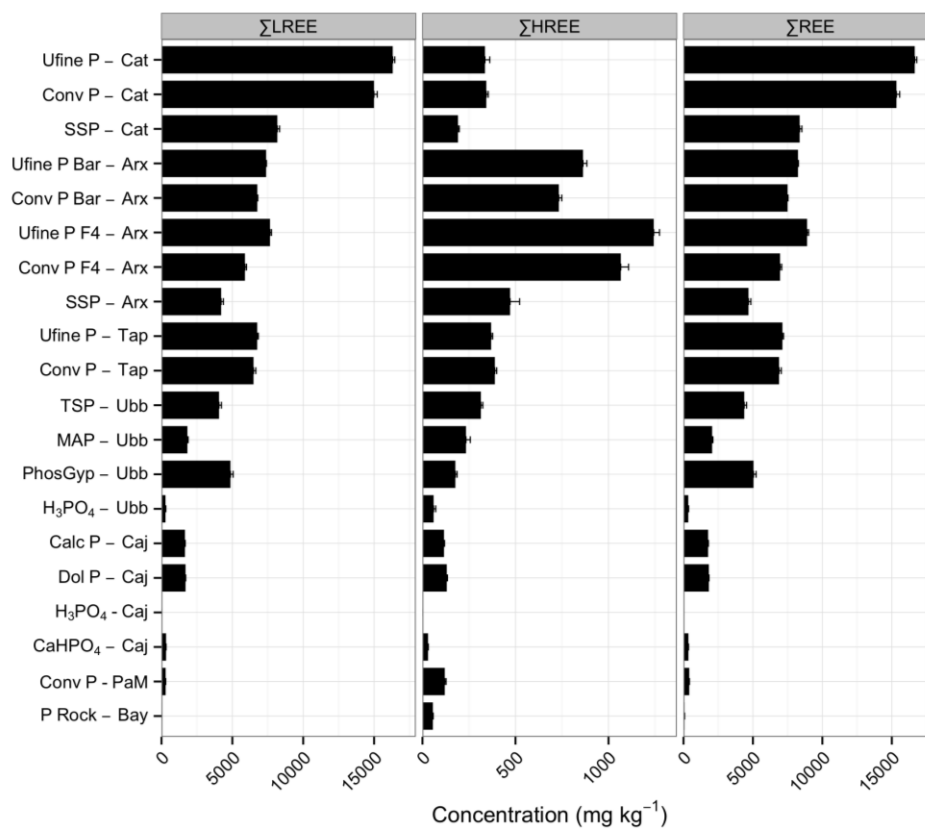
Fig. 2.

Sum of light rare earth elements ($\sum$LREE), heavy rare earth elements (($\sum$HREE), and total REE (($\sum$REE) of 20 samples of processed raw materials and products from phosphate fertilizer industry.
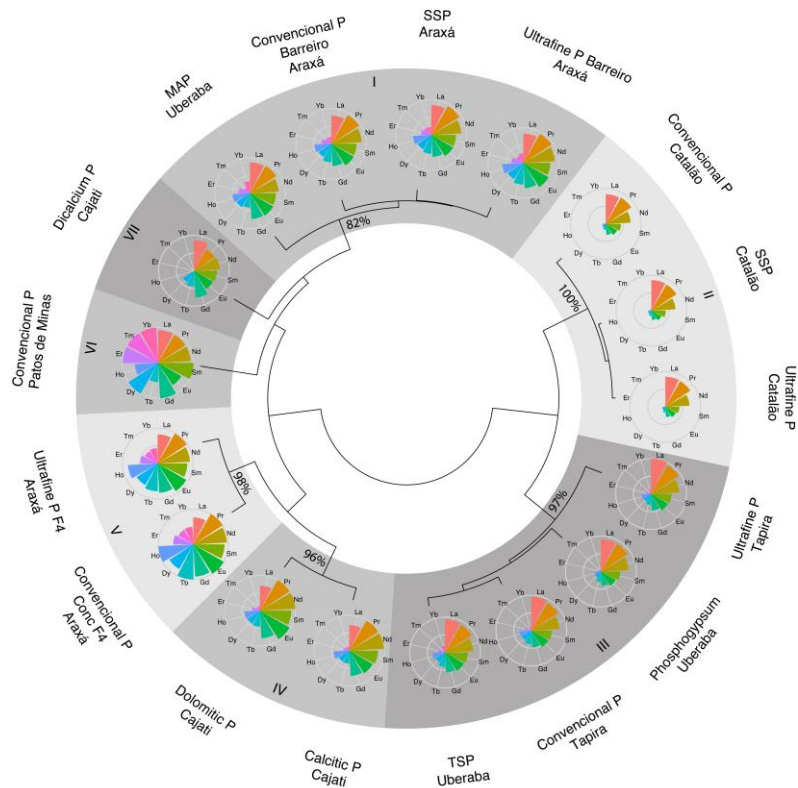
Fig. 3.

Clustering of samples of raw materials and products from phosphate fertilizer industry based on their REE contents normalized by their respective Ce content. Groups are indicated with Roman numerals (I-VII) and their bootstrap support (1,000 bootstrap replicates) are shown in the respective branches. The radar charts at the tip of terminal branches display the ratio REE/Ce for each sample rescaled to vary between 0 and 1 (maximum across all samples).
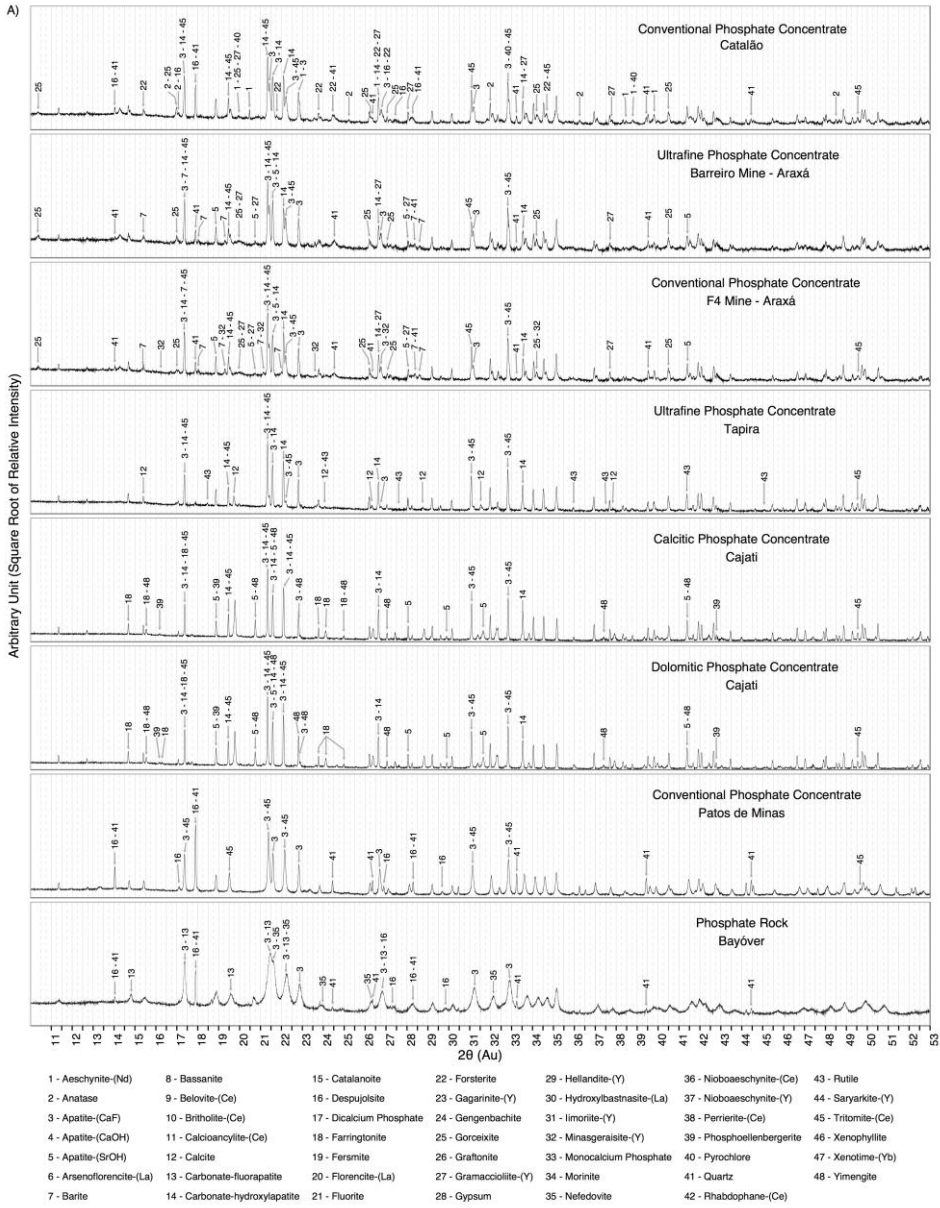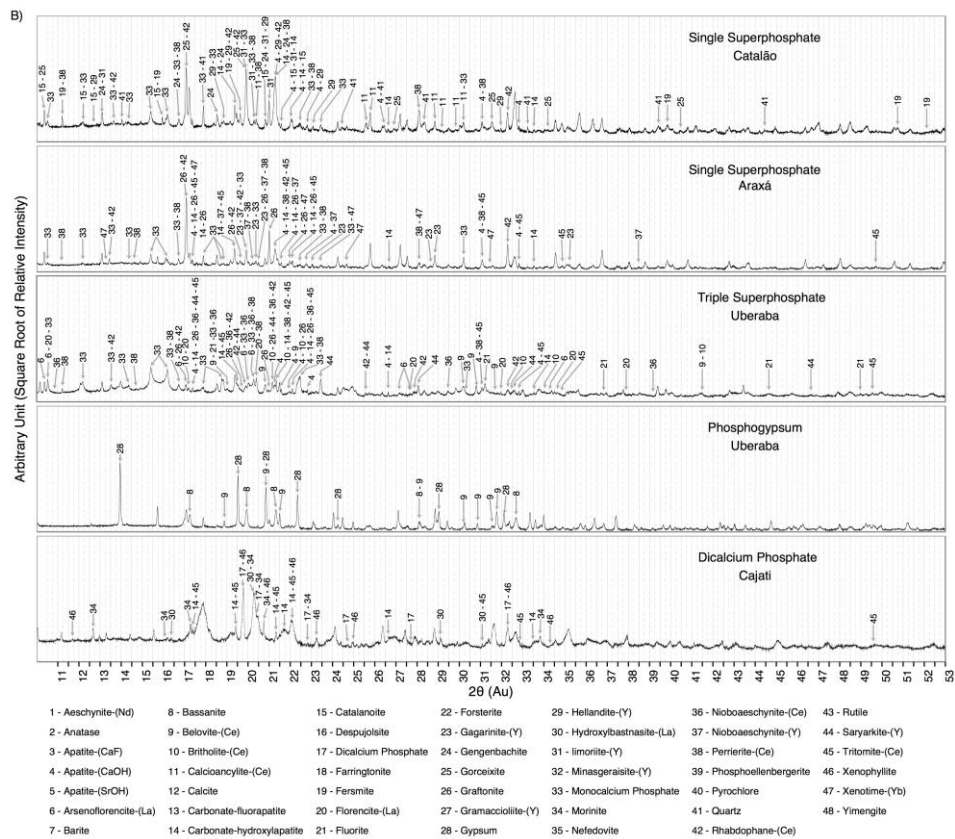
Fig. 4.

Synchrotron-based X-ray diffraction patterns of A) raw materials and B) products of phosphate fertilizer industry in South America. Peaks are identified by numbers indicating their associated crystalline phases according to the list at the bottom of each subfigure. Chemical compositions for these crystalline phases are given in Table S1.

PAPER 2

Rare earth elements (REY) sorption on soils of contrasting mineralogy and texture.

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Abstract

Rare earth elements (REY) are the lanthanide elements (Z = 57-71), which have an ever-growing presence in present-day industries, agriculture, and in modern life. Consequently, environmental concentrations are expected to increase accordingly as a result of intensified utilization. Soils are an important sink for REY elements, yet little research has been conducted concerning activity, inputs, and lability in soil systems. This study evaluated the REY (lanthanides + yttrium) sorption and partition coefficients (K_d) in two broadly representative soils, with contrasting mineralogy and organic character, formed under distinct environmental conditions: an Oxisol from Brazil and a Mollisol from the USA. Batch reactions of soils suspended in a background electrolyte solution of 5 µmoles kg^{-1} of $Ca(NO_3)_2$ at 1:100 solid to solution were reacted with 80 µmoles kg^{-1} REY added individually and in multi-REY competitive systems to evaluated adsorption after 3h and 72h over a wide pH range (from ~2 to ~8). Results showed sorption was similar for all REY within each soil type when pH was held near the natural measured soil pH; Mollisol pH 6.85, Oxisol pH 4.35. However, REY sorption (by K_d) was nearly two-fold greater in the Mollisol compared to the Oxisol for the single REY experiments. Mutli-REY competitive sorption reactions showed a decrease in K_d for both soils at 3 and 72 h, and to a greater extent for the Mollisol, indicating soil type had a strong effect on the sorption affinity of each REY. It was also observed that REY sorption increased from low to high pH (pH 2-8) in the Oxisol, and increased with pH from 2 up to the point zero charge (PZC) in the Mollisol, but then stabilized. The varying REY K_d values from these two distinct and abundant soils, with and without REY competition, and over a range of pH are explained in terms of soil mineralogy (i.e., 2:1 clays in the Mollisol; oxides in the Oxisol) and organic matter content. Our findings show soil characteristic controls sorption, precipitation, and cation exchange capacity, which are the key mechanisms for predicting REY fate and transport in the environment.

Keywords: Rare earth elements, sorption, soil, partition coefficient.

1 –Introduction

Rare earth elements (REY) are a group of 17 elements with similar physicochemical characteristics, from which 15 belong to the lanthanide's group (from lanthanum to lutetium, Z= 57-71) and two in a group-3, scandium (Sc, Z=21) and yttrium (Y, Z=39) (IUPAC, 2005). According to their elemental densities, they are generally classified as light (LREY - La-Eu + Sc) and heavy (HREY - Gd-Lu + Y) (Dołęgowska and Migaszewski, 2013). It is also common to refer to Sm, Eu, and Gd as medium-MREY (Henderson, 1984), due to the lack of an absolute periodic classification for each element within the general groupings.

Environmental concentrations of REY have been increasing, principally due to their increased uses in modern-day tech-industries, agriculture, and in everyday life (El-Ramady, 2010). Anthropogenic activities, including phosphate fertilizer application and improper e-waste disposal have been implicated as substantive causes of REY addition in to soils (Zhang and Shan, 2001; Aubert et al., 2002; Hu et al., 2006; Laveuf and Cornu, 2009a; Smidt et al., 2011; Ramos et al., 2016). The impetus for investigating REY contents, inputs, and behavior in the environment and agroecosystems derives from their increased presence in modern-life.

Whereas REY are neither considered essential for life, nor toxic for the environment (Tyler, 2004), there remains a lack of ecotoxicological studies for REY. Even with the increasing use of REY in modern society, many questions concerning the biological and ecological roles of REY remain unanswered (Ramos et al., 2016). Studies have shown rare-earth pneumoconiosis, chronic toxicity, and negative influences on liver function (Sabbioni et al., 1982; Zhang et al., 2000; Zhu et al., 2005; He et al., 2008; Censi et al., 2011; Li et al., 2013; Ramos et al., 2016). Soils provide the growth medium for our foods, therefore soil REY contamination becomes a potential route for exposures in human populations.

REY reference values in soils have been reported broadly across the Earth's surface (Yoshida et al., 1998; Yamasaki et al., 2001; Takeda et al., 2004; Sadeghi et al., 2013; Sá Paye et al., 2016; Ramos et al., 2016), yet few studies have addressed REY sorption onto soils, which is relevant for predicting mobility and availability of potential emerging contaminants in the environment. Sorption at soil surfaces is an important physico-chemical process affecting lability and bioavailability of different elements in the environment. It is widely known that soil properties and the soil solution composition affect metal sorption (Alloway, 1990). REY sorption in soils is influenced by clay type and content, and to a greater extent, by alumino-silicates and oxides of iron and manganese (Pang et al., 2002). Studies have addressed the magnitude and mechanisms for REY sorption on specific surfaces (Bruque et al., 1980; McBride, 1980; Bonnot-Court and Jaffrezic-Renault, 1982; Miller et al., 1982; Miller et al., 1983; Laufer et al., 1984; Olivera Pastor et al., 1988; Maza-rodriguez et al., 1992; Fendorf and Fendorf, 1996; Aja, 1998; Takahashi et al., 1999; Xiangke et al., 2000; Coppin et al., 2002; Yoon et al., 2002; Kang and Hahn, 2004; Ridley et al., 2005; Davranche et al., 2005; Quinn et al., 2006; Wan and Liu, 2006; Piasecki and Sverjensky, 2008). However, most of the experiments were

conducted under highly specialized and specific conditions, for example, on controlled and simplified surfaces, with specific organo-mineral phases, over narrow and specific pH, and as single REY sorbates. Although important, these studies may not represent REY adsorption in natural soils, which are complex and heterogeneous systems with many mineral and organic phases. Due to the complexity of soil, it was important to perform REY adsorption experiments using specific and isolated solid phases, but now is important to follow those studies using complex soil samples and the suite of REYs as they are generally observed in the environment.

Mollisols and Oxisols are the most common soils in USA and Brazil, respectively (Schaefer et al., 2008; Liu et al., 2012). Mollisols account for more than 21% of the soil in the US (Soil Survey Staff, 2010), and Oxisols cover more than 38% of Brazil (Ker et al., 2012), being close to 46% in the Cerrado region (Lopes and Guilherme, 2016). It is well known that each forms under different environmental conditions, i.e. mid-latitude highly productive high-organic grasslands (Mollisol) and tropically derived highly weathered-leached and relatively oxide-rich soils (Oxisols). Therefore, they have significant physicochemical differences in their mineralogy, cation exchange capacity, type and, organic matter (OM) content. Because of the few studies evaluating REY sorption on natural soils, these two Orders with known differences and great territorial relevance are excellent candidates for REY sorption studies (Clark et al., 1998; Li, 2001; Cao et al., 2001; Pang et al., 2002; Tang and Johannesson, 2005; Tang and Johannesson, 2010b).

This study evaluated lanthanides+Y (hereafter REY) adsorption on an Oxisol from the Brazilian Cerrado and on a Mollisol from a semi-arid region in the United States under varied experimental conditions including REY competition and over a range of pH. Time-reactions of 3 and 72 h of equilibration were assessed. Batch adsorption experiments were carried out on individual REY (single element) and in competitive REY (all REY) systems under at the soils' natural measured pH conditions and over a pH range from <2 to >8. The role of REY in the environment is a matter of continued research, and information provided by this study will elucidate REY sorptive behavior in two important natural soil orders, while offering useful information for environmental management planning and plant nutrition studies (Ramos et al., 2016).

2 - Materials and Methods

2.1 - Soil Samples and Sampling

The A horizons of the two mineralogically different soils were collected in areas of native vegetation in the US and Brazil, i.e., both sites had no records of anthropic intervention. The soils were previously classified according to the US Soil Taxonomy (Soil Survey Staff, 2010) as Mollisol (USA) and Oxisol (Brazil). The US Mollisol was collected from a zero order basin of the *La Jara* catchment on the East Fork *Jemez* River watershed within the Valles Caldera National Preserve, part of the Critical Zone Observatory (New Mexico, USA) (Figure 1-A). Sampling of the Brazilian soil was performed in a Natural Preservation Area of coffee farm located in the municipality of São Roque de

Minas, in the physiographic region of the Alto São Francisco (Minas Gerais - Brazil) (Figure 1-B). Both samples were air-dried and sieved to 2-mm prior to further analysis. Other details about soil sampling can be found in Vázquez-ortega et al. (2015) and Carducci et al. (2015).
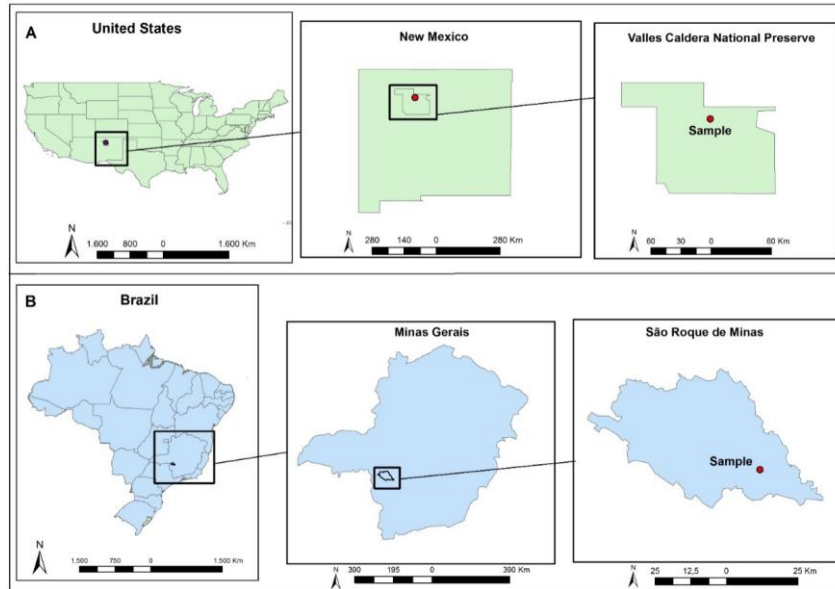

Figure 1.A – Valles Caldera National Preserver, New Mexico – USA. B – São Roque de Minas, Minas Gerais – Brazil.

2.2 - Soil Characterization

The air-dried and sieved samples were digested by means of an alkaline fusion method at the Arizona Laboratory Emergent Contaminants (ALEC). Aliquots of 0.0500 ± 0.0001 g from each sample were fused with 1.5000 ± 0.0001 g of flux (lithium metaborate-tetraborate) in platinum crucibles at $1000°C$ (Katanax, SPEX Sample Prep, Metuchen-NJ). The cooled pellet was dissolved in 50 mL of 10% HNO_3 at $120 \pm 20°C$ with magnetic stirring for complete solubilization. Samples were diluted in 2% HNO_3 for analysis. Elemental concentrations in the digested solutions were determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent,7700x with ASX 500 autosampler). Certified reference materials (OREAS Research exploration® 100, 100a, and 100b) and blank samples were digested for quality control. The oxides abundances were assumed from ICP-MS results (by molar ratio). The mean REY concentrations of the standard reference materials obtained by ICP-MS and their respective mean recoveries are presented (Table 1). For the Oxisol, particle size analysis was performed by employing slow agitation of the soil suspension containing NaOH 1 mol kg^{-1} for 16 h according to Vettori, L. (1969). The percentage of size-class fractions in a Mollisol sample was determined using ASTM C 1070–01 test (ASTM, 2000).

High temperature oxidation followed by infrared detection of CO_2 was used to determine total organic carbon (TOC, Shimadzu TOC-VCSH analyzer with solid state module SSM-5000A, Columbia, MD). Cation exchange capacity (CEC = $\sum$ Ca^{2+}, Mg^{2+}, K^+, Na^+, H^+, Al^{3+}) at the natural measured pH, at pH 7.0, and ΔpH were calculated according to the method described in Vettori, L.

(1969). The point of zero charge (PZC) was estimated by PZC = 2 pH KCl − pH H_2O (pH KCL = 1:25, v/v, solution 1 mol.L^{-1} KCl / soil; pH H_2O = 1:25, v/v water/soil) according to Keng and Uehara (1973).

The mineral phases in both soils were evaluated by X-ray diffraction (XRD) using synchrotron light source (Stanford Synchrotron Radiation Lightsource, Stanford, CA). Powdered samples were dispersed on low background adhesive tape with XRD collected in transmission at 0.9765 Å, diffractograms were calibrated with a LaB_6 standard and converted to Cu K-α wavelength using non-linear curve fit and the Bragg equation. Mineral identification was performed using the Philip's X'pert HighScore Plus program (version 2.2a).

Table 1: REY certified and determined concentrations, and recoveries found for certified reference materials of the OREAS Research exploration® 100, 100a, and 100b.

REY	Certified value (mg kg^{-1})			Obtained value (mg kg^{-1})			Mean recovery (%)		
	*	**	***	*	**	***	*	**	***
La	260	816	789	230	842	739	89	103	94
Ce	463	1396	1331	412	1437	1262	89	103	95
Pr	47.1	134	127	42.1	135.9	118.4	89	101	93
Nd	152	403	378	123	368	323	81	92	86
Sm	23.6	48.8	48	21.7	52.1	45.5	92	107	95
Eu	3.7	8.1	7.8	3.3	8.5	7.4	90	105	95
Gd	20.3	42	40	18.8	35.3	31.2	93	84	78
Tb	3.8	5.9	5.4	2.9	4.1	3.6	75	69	67
Dy	23.2	33.3	32.1	21.1	34.0	30.3	91	102	94
Ho	4.8	6.5	6.3	4.6	6.9	6.2	95	106	98
Er	14.9	19.5	18.7	14.1	20.4	18.4	94	104	98
Tm	2.3	2.9	2.7	2.1	3.0	2.7	93	103	101
Yb	14.9	17.5	17.6	14.0	19.2	17.3	94	110	98
Lu	2.3	2.7	2.6	2.1	2.7	2.5	92	103	97
Y	95.5	135	133	121	178	160	127	132	120

*, **, and *** are certified reference materials OREAS Research exploration® 100, 100a, and 100b, respectively.

2.3 - REY Adsorption - Batch Test

To examine REY adsorption, experiments were performed at the natural soil pH (determined in 5 mmol kg^{-1} $Ca(NO_3)_2$, soil:solution of 1:100, n=5) and at values ranging from pH 2-8. Specific parameters for each experiment are described. The first experiment sought to evaluate REY adsorption in both soils at natural pH, simulating what would happen under undisturbed conditions. The second

experiment evaluated REY adsorption across a range of pH to verify possible influence on REY-adsorption due to aqueous REY speciation and pH dependent surface charge. In both experiments, 0.3 g soil was suspended and equilibrated in a 30 g background solution of 5 mmol L^{-1} $Ca(NO_3)_2$ (pH = 5.5, ionic strength 15 mmol kg^{-1}) for 72 hours (time 0 h). After the initial equilibration, specific volumes of REY were added to 80 μmoles kg^{-1}, which is the initial concentration for the sorption reactions. The REY were added individually as nitrate salts and in a multi-REY mixed cocktail (all REY at the same conc. mixed in the same tube). The suspensions were agitated for 3h and 72h time-steps, then centrifuged for 10 min at 14,000 rpm and filtered (0.45 μm GHP). Blank controls were performed to examine possible contamination and REY-desorption from the soils. These control blanks were REY-FREY$_{blank}$ (rare earth elements free, soil + background solution only) and Soil-FREY$_{blank}$ (no soil, rare earth elements + background solution only). REY certified standards were used to prepare all REY solutions with 5 mmol kg^{-1} $Ca(NO_3)_2$. The REY contents in the equilibrium concentration were determined by ICP-MS. Details on the K_d batch tests followed USEPA (1999). Calibration standards for each REY were prepared matching the matrix composition with samples diluted for ICP-MS analysis in order to account for matrix interferences. The detection limits in ng kg^{-1} were for Y(0.1), La(0.4), Ce(0.02), Pr(0.4), Nd(0.7), Sm(0.1), Eu(0.6), Gd(0.1), Tb(0.01), Dy(0.1), Ho(0.1), Er(0.1), Tm(0.1), Yb(3.7), and Lu(10.2).

2.3.1-REY adsorption in natural pH

The natural pH for both soils was determined; 6.75±0.07 and 4.4±0.08 for the Mollisol and for the Oxisol, respectively (in 5 mmol L^{-1} $Ca(NO_3)_2$, soil:solution of 1:100, n=5). The batch test experimental parameters previously described were used for REY adsorption. The experimental matrix included 16 individual REY, 1 cocktail REY, 1 REY-FREY$_{blank}$, 1 Soil FREY$_{blank}$, 2 time-steps all in triplicate (n=114). Suspensions were left shaking in two durations, 3 and 72 hours, with the last one comprising the REY alternate cycles of 12 h of shaking and 12 h of resting. Shortly after the addition of REY and after shaking, the pH was measured in each tube. After each time-reaction, the equilibrium concentration was measured (following the batch test parameters above) by ICP-MS.

2.3.2 -REY adsorption in different pH values

Two solutions with 15 mmol kg^{-1} HNO_3 and 5 mmol kg^{-1} $Ca(OH)_2$ (ionic strength = 15 mmol kg^{-1}) were prepared for pH adjustments. The pH was adjusted to a wide range of pH values, ranging from pH<2; 2<pH<2.5; 2.5<pH<3; 3<pH<3.5; 3.5<pH<4; 4<pH<4.5; 4.5<pH<5; 5<pH<5.5; 5.5<pH<6; 6<pH<6.5; 6.5<pH<7; 7<pH<7.5; 7.5<pH<8; to pH>8. Experimental parameters of the batch test were used as described in item 2.3. Adsorption reaction time of all REYs (individual and as cocktail) was 3 hours. Then, the solution was collected for ICP-MS analyses.

2.4 –Adsorption and parameters for species models – K_d and Q

2.4.1 – Model Parameters

For all experiments, the REY concentrations were calculated on a mass basis. Equation 1 shows REY adsorbed per unit weight of adsorbent:

$$Q = \frac{((C_i - (C_e - C_eREY - FREYblank)) * Vsol}{Msoil} \qquad \text{Eq. (1)}$$

where, Q is the REY adsorbed (μmoles kg^{-1}); C_i and C_e are the initial and the equilibrium REY concentrations in the solution (μmoles kg^{-1}), respectively; C_eREY-$FREY_{blank}$ is the equilibrium REY concentration obtained from the soil (desorption in μmoles kg^{-1}); V is the volume of the solution (mL); and M is the mass of the adsorbent (g).

The values of the distribution coefficient (K_d) in kg kg^{-1} were calculated as shown in equation 2:

$$Kd = \frac{Q}{Ce} \qquad \text{Eq. (2)}$$

Where, K_d is the distribution coefficient (kg kg^{-1}); Q is the amount of REY adsorbed by the soil mass (μmoles kg^{-1}); and C_e is the equilibrium REY concentrations in solution (μmoles kg^{-1}).

2.4.2 - Parameters assumed in modeling REY adsorption on soils

Predicted thermodynamic aqueous and solid phase REY speciation was evaluated using Geochemist's Workbench (Bethke, 2007) with the Lawrence Livermore National Laboratory thermodynamic database (thermo.com.v8.r6+; Delany and Lundeen, 1990). To model the interactions of REY with soil surfaces over relevant pH ranges, the geochemical speciation of each REY was calculated in a background electrolyte solution of 5 mM $Ca(NO_3)_2$, $f(CO_2) = 10^{-3.5}$, and $f(O_2) = 10^{-0.7}$.

3 - Results

3.1 - Soil characterization

The REY concentrations in all standard reference materials used in this study are shown (Table 1). Recoveries for all REY were considered satisfactory, indicating QA/QC protocols assured data accuracy for REY analyses. Data concerning chemical and physical analyses (e.g. pH, CEC, texture, etc.) of both soils are shown and highlight that soil characteristics are quite different between the evaluated soils (Table 2). It is noteworthy that the OM content found for the Mollisol is approximately 10 times greater than the Oxisol, which influences the surface charge in each soil. Both soils have a predominantly negative surface charge, ΔpH values were negative, the Mollisol being more negative (-1.65) compared to the Oxisol, which is related to its mineralogy and OM content. The soil properties also influence CEC (natural pH and at pH 7.0) and PZC. The Mollisol showed lower PZC and higher CEC - especially ECEC - than the Oxisol, which is anticipated from the kaolinite and oxidic mineralogy.

Potassium oxide and sodium oxide in the Mollisol were 2.66 and 2.10 %, respectively. This fact is related to the presence of less-weathered minerals, which may also increase the net negative charge of the soil. This was confirmed by XRD analyses shown in figure 2-B, where the Mollisol

shows the following minerals: albite ($NaAlSi_3O_8$), anorthite ((Ca,Na)(Al,Si)$_4O_8$), augite ($Ca(Mg, Fe, Al)(Si,Al)_2O_6$), kaolinite ($Al_2Si_2O_5(OH)_4$), Illite ($K,H_3O$)($Al,Mg,Fe$)$_2$($Si,Al$)$_4O_{10}[(OH)_2,(H_2O)]$, orthoclase ($KAlSi_3O_8$), and quartz ($SiO_2$). By contrast, iron and aluminum oxides as well 1:1 clay (kaolinite) were the main mineralogical phases identified for the Oxisol, indicative of its high level of weathering-leaching compared with the Mollisol (Figure 2). Total REY contents found for both soils are also shown, LREY contents in the Mollisol were higher than those found in the Oxisol, except for cerium and the HREY contents were higher in the Oxisol than those of the Mollisol (Table 2). Among all REY, cerium was the element with the highest concentrations in both soils.

Table 2. Chemical and physical characteristics of the evaluated soils.

Element		Unit	Soil	
			Mollisol	Oxisol
O.C.		g kg^{-1}	14	2.26
pH$_{H2O}$			6.85	4.35
pH$_{KCl}$			5.2	4.25
Δ pH			-1.65	-0.1
PZC			3.55	4.15
CEC		cmol$_c$ dm^{-3}	11.64	10.22
ECEC			9.69	1.75
Oxides	SiO$_2$	%	51.8±3	18.3±0.5
	Al$_2$O$_3$		8.1±0.5	34.6±0.9
	Fe$_2$O$_3$		1.38±0.1	14.1±0.4
	TiO$_2$		0.48±0.1	1.5±0.2
	K$_2$O		2.66±0.1	0.4±0.1
	Na$_2$O		2.1±0.2	0.5±0.1
REY	La	mg kg^{-1}	22.46±1.5	3.27±0.9
	Ce		42.13±2.9	106.1±9.2
	Pr		4.73±0.3	0.89±0.2
	Nd		14.84±1.3	3.19±0.9
	Sm		3.01±0.2	1.15±0.3
	Eu		0.59±0.1	0.38±0.1
	Gd		1.99±0.1	2.52±0.5
	Tb		0.43±0.1	0.48±0.1
	Dy		2.66±0.1	4.60±1.2
	Ho		0.60±0.1	1.06±0.3
	Er		1.75±0.1	3.29±0.8
	Tm		0.33±0.1	0.54±0.1
	Yb		1.94±0.1	3.39±0.8
	Lu		0.35±0.1	0.55±0.1
	Y		14.43±0.1	27.29±6
LREY/HREY			3.6	2.6
Texture	Sand	%	46	3
	Silt		38	15
	Clay		16	82

pH$_{H2O}$ - 1:2.5 Soil:Water - v/v;
pH$_{KCl}$ - 1:2.5 Soil:1M KCl - v/v
ΔpH= pH$_{KCl}$ - pH$_{H2O}$; n=5;
PZC = 2 pH$_{KCl}$ - pH$_{H2O}$;
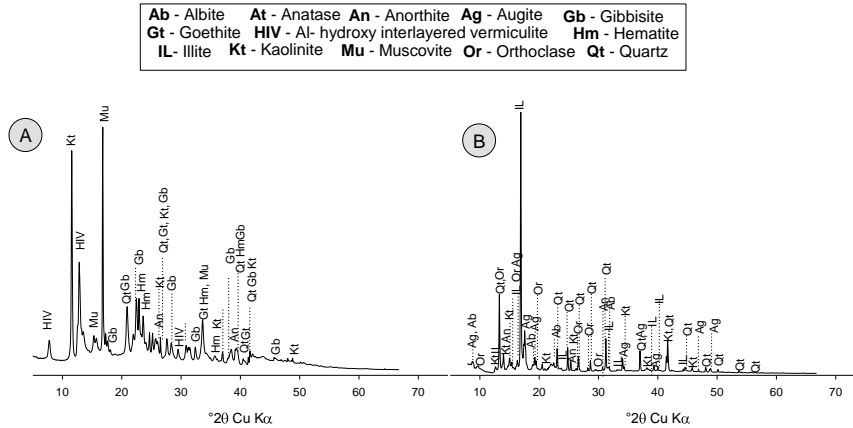Error bars for oxides and REY were from n=3

Figure 2: X-ray diffractograms for Oxisol (A) and Mollisol (B). Oxisol minerals - Anatase (TiO$_2$), Al-Hydroxy interlayed Vermiculite (Mg;Fe$_3$Al)$_3$(Si; Al)$_4$O$_{10}$(OH)$_2$4H$_2$O, Gibbsite (Al(OH)$_3$), Goethite (Fe$_3$OOH), Hematite (Fe$_2$O$_3$), Kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), Muscovite KAl$_2$(Si$_3$Al)O$_{10}$(OH,F)$_2$) and, Quartz (SiO$_2$). Mollisol minerals - Albite (NaAlSi$_3$O$_8$), Anorthite ((Ca,Na)(Al,Si)$_4$O$_{8,}$) Augite (Ca(Mg, Fe, Al)(Si,Al)$_2$O$_6$), Kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), Illite (K,H$_3$O)(Al,Mg,Fe)$_2$(Si,Al)$_4$O$_{10}$[(OH)$_2$,(H$_2$O)], Orthoclase (KAlSi$_3$O$_8$) and, Quartz (SiO$_2$).

3.2 - REY Adsorption

3.2.1-REY adsorption in natural pH

Figure 3 shows the REY (under single and cocktail REY treatments) adsorption results for both soils (A and B – Oxisol, C and D – Mollisol) for the two studied time-reactions (3 and 72 hours). Note that both soils adsorbed higher amounts of all REY following the single element addition compared with the competitive system (cocktail); the REY adsorption in both soils was 2-3x greater in the single than in the cocktail (multielemental) system. The REY adsorption on the Oxisol increased with increasing reaction time from 3 to 72 h, while the Mollisol exhibited the opposite trend where adsorption decreased with increasing the reaction time. The pH was measured in each tube at both time steps and in general the pH of the soil suspension decreased over time for the Mollisol (~one pH unit) but remained steady (only ~0.1 pH units) for the Oxisol (Table 3).

The decrease in the REY sorption for the Mollisol with increased reaction time prompted the analysis of aluminum in solution, as a possible explanation, in select samples over the REY-series for both time points. Those with Al analysis included the following treatments: La, Ce, Gd, Lu and REY-FREY$_{Blank}$. Exchangeable Al was also determined for comparative purposes according to Sparks (1996). The results for Al content and exchangeable Al for the chosen treatments are shown (Figure 4). Tukey's tests were performed at 0.05 level of significance in order to compare Al concentration and exchangeable Al among REY-treatments. Aluminum values found for any REY-treatment after 3 or 72 hours of reaction were significantly higher than the exchangeable Al and the REY-FREY$_{blank}$, except for the Lu REY-treatment, which showed no difference from exchangeable Al, for 3 hours of shaking.

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This may account for the higher adsorption after 3 hours as compared with that observed after 72 hours and also partially explain the decrease in pH of the solution over time observed only for the Mollisol (Table 3). As shown in figure 2-B, the Mollisol has as its main mineral phases some that contain Al in their crystal structures, e.g. kaolinite, anorthite, augite, albite, illite, and orthoclase. It is possible that the REY applied to the waetherable Mollisol may have exchanged over time with Al present, the same Al concentration was not detected in REY-FREY$_{blanck}$ and the exchangeable Al was lower than the Al released in the REY treatments following the adsorption of the REY. Al-hidroxide interlayer vermiculite mineral found for Oxisol can also release Al from the octahedral interlayers and decrease the pH solution forming gibbsite, consequentely. However, it was not observed in this experiment.

In general, REY adsorption in the Mollisol was higher than in the Oxisol, and the LREY were adsorbed to a greater extent on both soils. For the Mollisol, Eu had the greatest adsorption values, while Y was lowest.
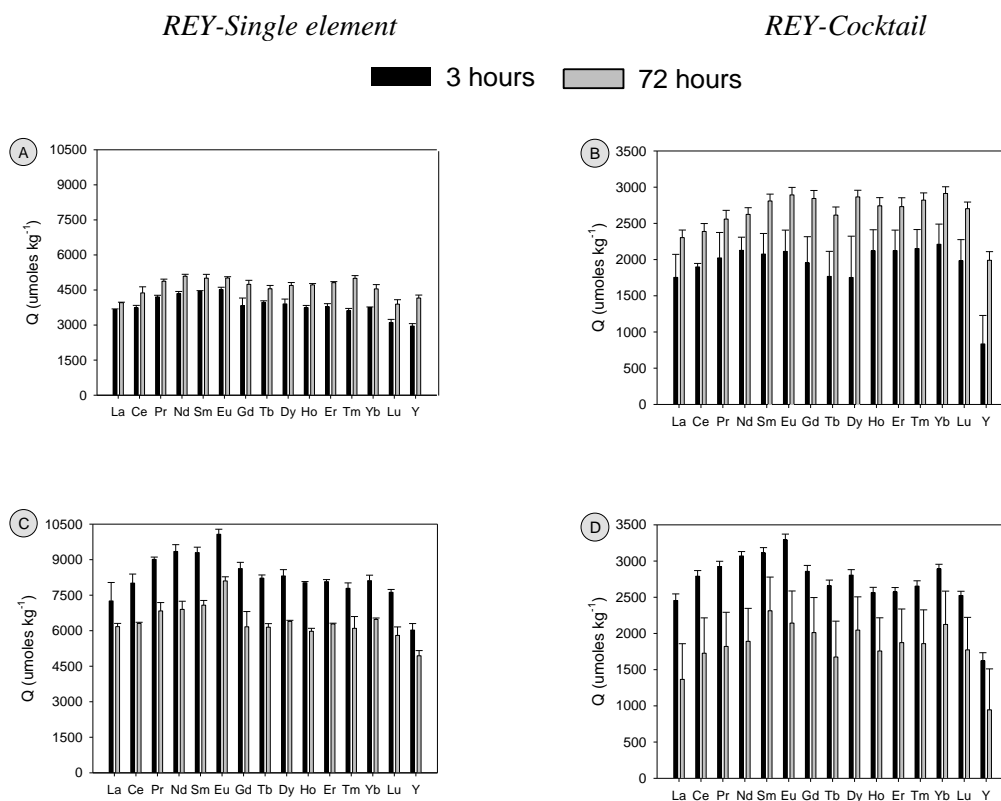

Figure 3: Adsorption of REY on single and multielemental (cocktail) systems in the Oxisol (A and B) and the Mollisol (C and D) for both reaction times (3 and 72 hours) and natural pH.

Table 3. Average for pH values found after different time reactions following REY-adsorption on the Oxisol and the Mollisol.

REY	Soils			
	Oxisol (pH$_{inicial}$ 4.35)		Mollisol (pH$_{inicial}$ 6.85)	
	pH$_{3hours}$	pH$_{72\,hours}$	pH$_{3hours}$	pH$_{72\,hours}$
La	4.41±0.02	4.27±0.04	6.85±0.01	5.61±0.02
Ce	4.46±0.01	4.30±0.01	6.73±0.02	5.55±0.01
Pr	4.41±0.02	4.28±0.03	6.71±0.01	5.52±0.01
Nd	4.30±0.02	4.14±0.04	6.80±0.01	5.48±0.01
Sm	4.43±0.02	4.29±0.01	6.72±0.01	5.41±0.02
Eu	4.42±0.02	4.26±0.02	6.72±0.01	5.62±0.01
Gd	4.33±0.03	4.19±0.04	6.75±0.01	5.48±0.01
Tb	4.32±0.02	4.16±0.03	6.76±0.01	5.49±0.01
Dy	4.43±0.02	4.29±0.01	6.76±0.01	5.59±0.01
Ho	4.44±0.01	4.28±0.03	6.66±0.01	5.41±0.01
Er	4.41±0.02	4.27±0.02	6.67±0.02	5.42±0.01
Tm	4.39±0.02	4.16±0.02	6.72±0.01	5.49±0.01
Yb	4.38±0.01	4.21±0.03	6.56±0.08	5.47±0.01
Lu	4.38±0.05	4.22±0.03	6.70±0.04	5.40±0.01
Y	4.39±0.04	4.13±0.05	6.44±0.02	5.44±0.01
REY Cocktail	4.28±0.02	4.21±0.01	6.47±0.05	5.52±0.03
REY FREY	4.45±0.01	4.43±0.01	6.75±0.02	6.78±0.02
REY Soil FREY	5.45±0.02	5.46±0.02	5.44±0.02	5.48±0.02

pH$_{3hours}$ and pH$_{72hours}$ measured following the reaction time of 3 and 72 h, ±standard error of the mean, (n=3).

It was observed that REY adsorption trends were similar in both soils and reaction times, and K_d values have been calculated for comparison of the adsorption of all REY-singles sorbed on soils after 3 hours of reaction (Fig. 5). The thermodynamically predicted REY species expected in each soil were calculated. The K_d values for the Oxisol were lower than those found for the Mollisol (Fig. 3). However, the adsorbed REY species differed depending on the soil, attributed to the natural pH. For the Oxisol, REY were adsorbed as REY^{+++} and $REYNO_3^{++}$ species, which were the main species present in pH values around 4.5 (natural pH for the Oxisol). For the Mollisol, REY were adsorbed principally as $REY(OH)^{++}$ and $REY(CO_3)^+$. The highest adsorption on the Mollisol was Eu, possibly due to the tetravalent species ($REY_2(OH)_2^{++++}$) at the Mollisol natural pH, which is close to 6.85 (Fig. 5). Some of the observed REY-partitioning to the solid phase was not adsorption, but rather precipitation, again attributed to the natural pH for the Mollisol. It is thermodynamically predicted that at the pH values above 7-8 and REY activity modeled, most of the REY start to precipitate, especially the HREY.
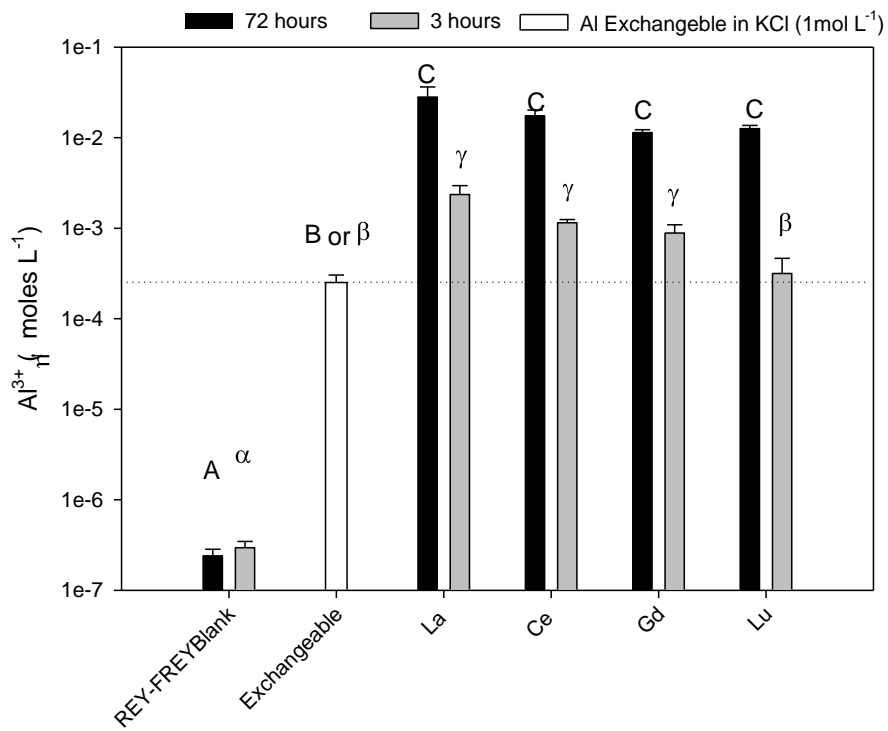
Figure 4: Aluminum in solution after both reaction times and exchangeable aluminum in the Mollisol. Exchangeable aluminum was measured according to Sparks (1996) (n=3). Values followed by the same Greek characters (3 hours) or Roman letters (72 hours) are not significantly different by Tukey's test at 0.05 level.

Figure 5: Effect of soil type on REY (single) distribution coefficient (K_d) in 3 hours (reaction time). REY species were determined using Geochemist's Workbench modeling software.

3.2.2-REY adsorption in different pH values

Results of REY adsorption capacity as a function of pH for both soils are presented (Fig. 6). Superimposed on this figure are the predicted species abunda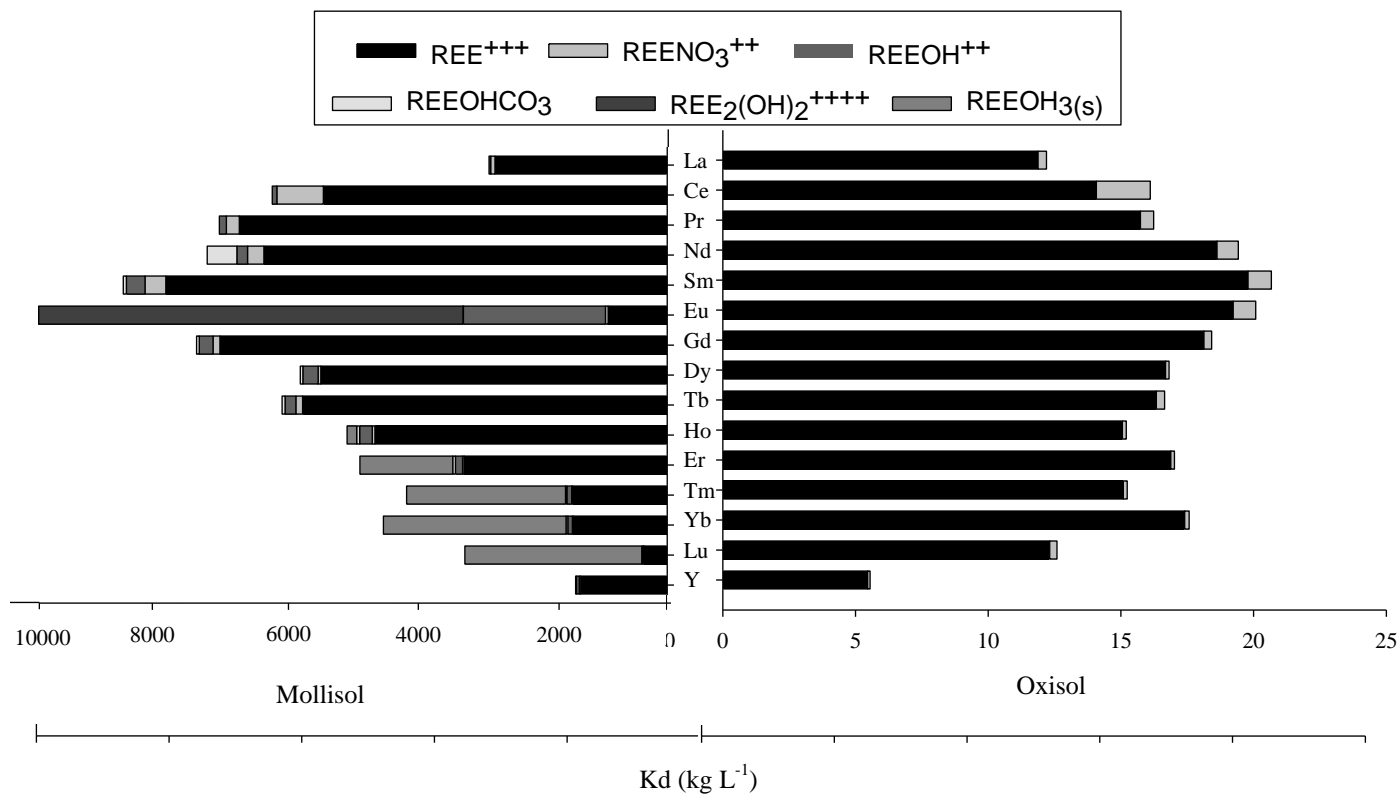nces of each REY present across the pH ranges examined. The dotted line in figure 6 indicates the point of zero charge (pzc) of the soils. In general, for the same soil, the REY-adsorption trends over the pH ranges were similar. The REY adsorption on the Mollisol was higher than in the Oxisol for all REY over the studied pH range. The maximum adsorption of REY in the Mollisol was at pH 3.5 to 4, after which it did not increase. On the other hand, the REY-adsorption on the Oxisol kept increasing over the entire pH range, with REY precipitation predicted above pH about 7 (depending on the REY), based on geochemical thermodynamic modeling.

For all REY-adsorption experiments, three different trends over pH values became evident for the Oxisol. Over the pH range evaluated, the main predicted REY species in solution were REY^{+++} and $REYNO_3^{++}$ (nitrate form), until their respective precipitation at ~pH > 7. Some forms of REY-carbonate were predicted, namely for LREY. Modeling did not show $Y(OH)_{3(s)}$ precipitation within the studied parameters. Moreover, it seems that species distribution did not interfere in the adsorption, except for Eu, which reached a high K_d for both soils when the $Eu_2(OH)_2^{++++}$ species was predicted to predominated in solution (higher than 50 %). This substantiates the results shown before for REY adsorbed on the Mollisol, where it was observed that the pH was a key variable, because Eu was the only REY that presented a bidentate tetravalent species. Moreover, the HREY species modeling showed that REY-precipitation should start below pH 7.0, which may have interfered with the adsorption values for HREY. Once again, the LREY had the highest adsorption for both soils followed by the HREY, over the studied pH range.
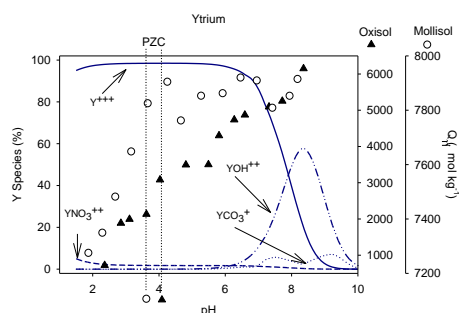
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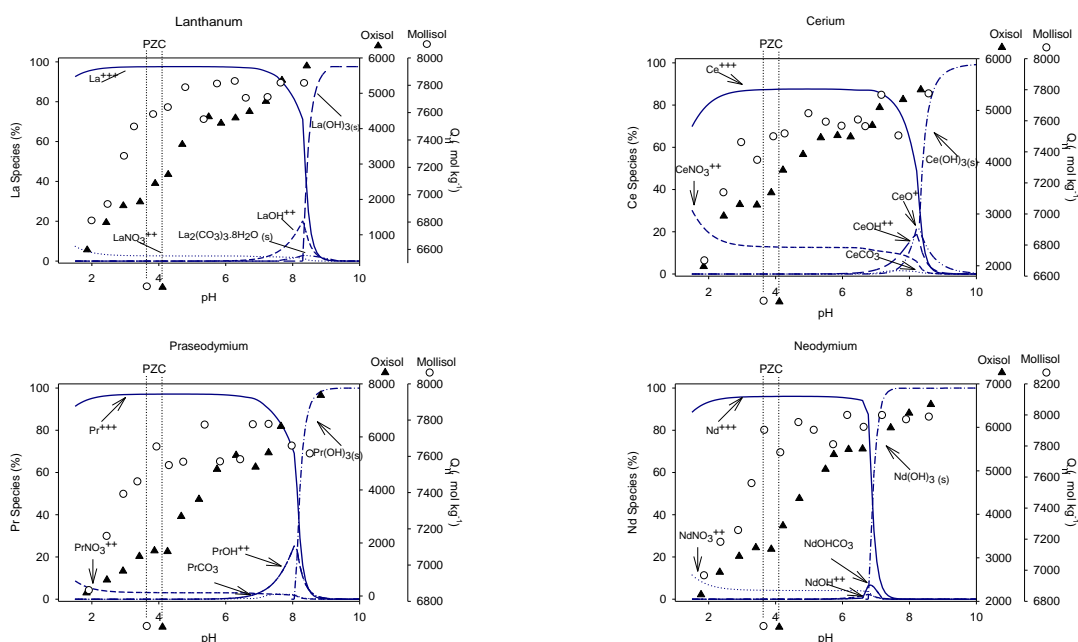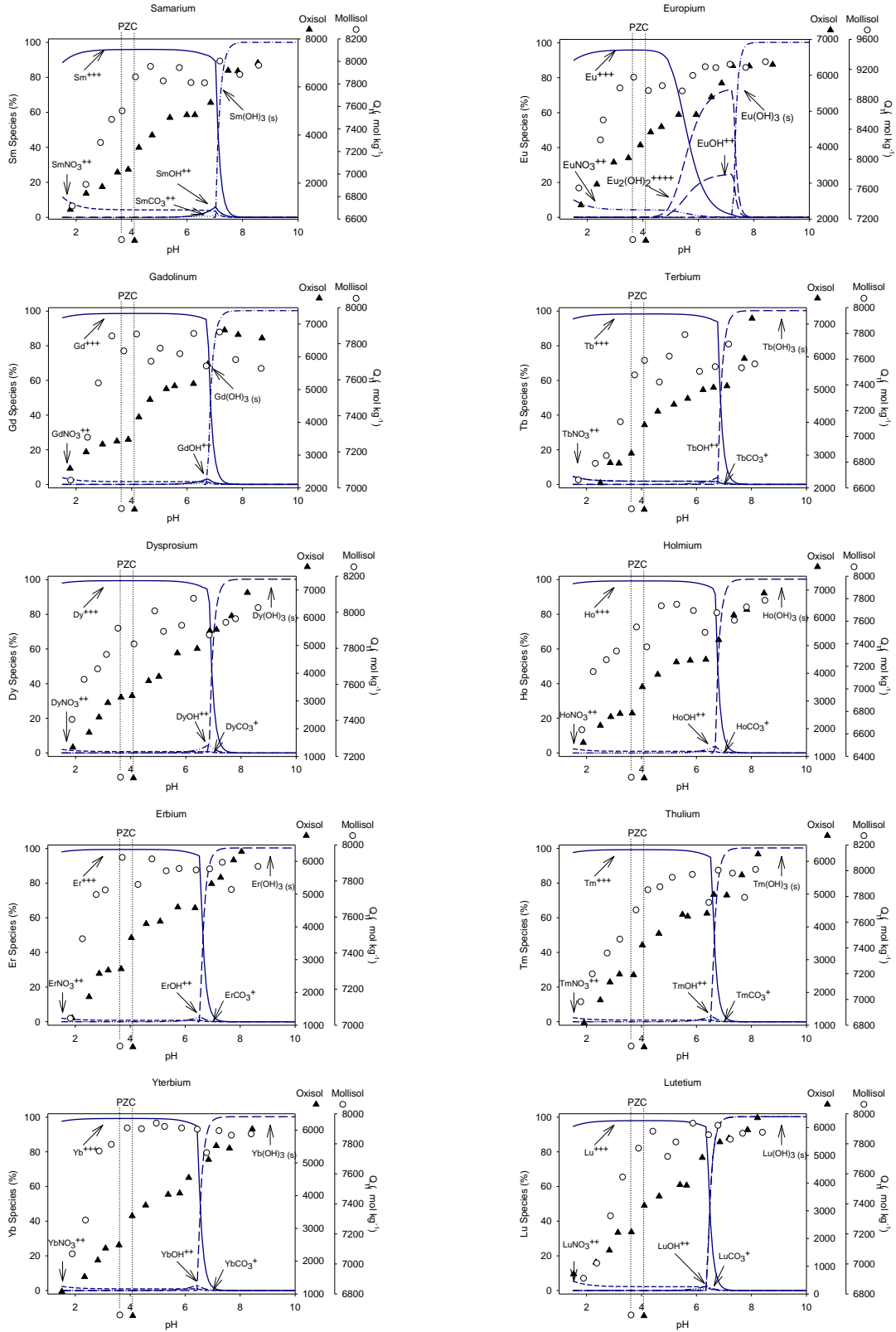
Figure 6: Effect of pH on each REY (singles) adsorbed on the Mollisol and the Oxisol and REY species in solution. REY speciation was determined using Geochemist's Workbench modeling software. The speciation was performed for all REY at 80 μmoles kg^{-1} with a background electrolyte of 5 mmoles kg^{-1} Ca(NO$_3$)$_2$, 1x10$^{3.5}$ moles kg^{-1} CO$_{2(f)}$ and 1x10$^{0.7}$moles kg^{-1} O$_{2(f)}$. Dotted lines represent the estimated pzc for both soils (Mollisol – circles; Oxisol – triangles).

Adsorption is shown for multielemental systems, i.e., REY-cocktail treatments, on the Oxisol and the Mollisol, for all studied pH ranges (Figure 7A-B). Highlighted sections of figure 7 show the predicted interaction of the REY with organic and mineral solid phases across pH ranges. The REY adsorption values were lower when all REY were used together, when compared with the adsorption found for single REY. This fact was due to higher ion concentration in solution and consequently less REY adsorption, i.e., due to competition for limited adsorption sites. The REY-trends over the studied pH range for each individual soil was similar. All these trends are similar to those shown before for REY-single treatment (Fig. 6).

The Mollisol competitive sorption is shown with two distinct uptake regimes with respect to pH, where REY adsorption increased up to the pzc 3.5-4, then leveled off (Fig. 7B). The same results were observed for the Oxisol, but with smaller intensity (Fig 7A). However, in addition to this bimodal trend to the pzc, the REY-adsorption on the Oxisol had additional K$_d$ trends at 4.0-6.2; 6.2-7.8; above 7.8. Adsorption was slightly higher for LREY than for HREY, as was also observed for the experiment with the soils' natural pH described above.
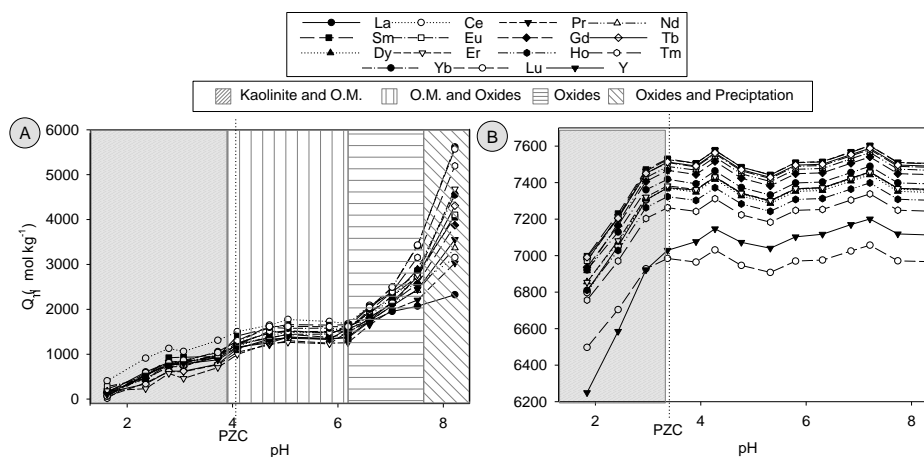
Figure 7: Effect of pH on REY (cocktail) adsorbed on the Oxisol (A) and the Mollisol (B). The highlighted sites are possible sources and/or interferences for soil charges and/or REY precipitation.

4 –Discussion

4.1 - Soil characterization

It is well known that the environmental factors contributing to soil formation differ significantly between tropical and temperate regions. Mollisols are formed under moderate climate, with pronounced seasonal moisture deficit, which helps retain weatherable minerals in the soil (Soil Survey Staff, 2010). This explains the types of minerals found for the Mollisol in this study (Figure 2-B). Conversely, Oxisols are formed in tropical and intertropical areas under severe weathering-leaching conditions, resulting in the removal of weatherable minerals and an residual accumulation of kaolinite and oxides (Kampf and Curi, 2003; Resende et al., 2011). Oxisol mineralogy consists of 1:1 clay minerals, such as kaolinite and oxides of Al and Fe such as hematite, goethite, and gibbsite (Curi and Franzmeier, 1984), consistent with the results found in this study (Figure 2-A). Soil genesis, a function of environmental conditions, explains the results for oxides and OM in each soil (Table 2).

In this study, soil samples from the Oxisol and the Mollisol were collected in areas selected for minmal anthropogenic interference. This allows for the quantification of background REY values (Juan, 1994) under the absence of human activities. In Table 2, the total REY values are shown (background values by alkaline fusion) for the studied soils. The REY levels corroborate with the values presented by Ramos et al. (2016) in a comprehensive review reporting worldwide background values for REYs in soils from 33 countries, USA and Brazil included. The difference for LREY and HREY total values between the soils found in this study are likely best explained by the differential transport of REY during weathering-leaching (Ling and Liu, 2002).

In the environment where Oxisols are formed, i.e. high temperature and precipitation and consequently high weathering-leaching, losses of cations are expected, with a consequent pH decrease, while the opposite occurs for Mollisol (CEC and pH - Table 2). This fact may explain the lower and

higher levels of LREY and HREY, respectively, for the Oxisol (except for Ce) when compared with the Mollisol. Sá Paye et al. (2016) found high cerium concentration in several oxidic soils in Brazil, which was verified in the present study. These authors attributed high Ce to the predominance of igneous rocks as soil parent materials. Additional details concerning the influence of weathering-leaching on the total REY levels in similar soils, as used in this study are presented by Sá Paye et al. (2016), as well as Vázquez-Ortega et al. (2015; 2016). As shown in Figure 6, at low pH, REY occurs mainly in the free ion from, while at pH above 6 REY species tend to complex, which is especially true for HREY. The solubility product of REY-hydroxides at 25°C decreases from La (Ks=1.0×10^{-19} mol L^{-1}) to Lu (Ks=2.5×10^{-24} mol L^{-1}) (Latimer, 1938). In addition, HREY release water molecules from the hydration sphere more easily than LREY due to ionic radius contraction with increasing atomic number (Coppin et al., 2002), which makes them more prone to complexation when compared with LREY (Laveuf and Cornu, 2009; Moldoveanu and Papangelakis, 2012).

Organic matter (OM) was higher for the Mollisol (Table 2). Due to climatic conditions of diagenesis, temperate regions, as those predominant in the genesis environment of Mollisols, tend to accumulate organic compounds, which together with clay minerals, are responsible for the negative charges present in these soils (Liu et al., 2012). However, despite the lower OM content for Oxisols, OM has an important role in these soils. For tropical soils, it is widely known that organic compounds are important because they interact with soil components, with significant impact on net electrical charges, CEC, among others parameters (Resck et al., 1999). Organic matter present in the Oxisol may be the reason why the REY-adsorption in the Oxisol reached values sometimes near those found for the Mollisol, as Oxisols are known to have low charge density in their clay minerals.

4.2 - REY Adsorption

4.2.1-REY adsorbed in natural pH

Similar trends across REY-adsorption were observed in both soils, regardless of the treatment at the natural pH (Fig. 3). This indicates that REY have the similar behavior independently of the soil features and of the presence of others ions. Due to this behavior, REY are widely studied in pedogenic processes (Caspari et al., 2006; Laveuf and Cornu, 2009; Cidu et al., 2013; Vázquez-Ortega et al., 2016). However, in spite of similar trends, adsorption values for REY-single and REY-cocktail treatments were different for the two soils. The REY-adsorptions for REY-cocktail treatments were lower due to the ion concentration and as a result of competition for adsorption sites. Similar results were reported by Quinn et al. (2004) and Tang and Johannesson (2010).

Soil characterization is important for understanding REY-adsorption on the studied soils. Mineral and organic soil characteristics are important because of their influence on REY adsorption behavior (Tyler, 2004). However, results showed higher REY-adsorption on the Mollisol, regardless of

the treatment (single or cocktail) (Fig. 3). This can be explained due to the Mollisol, OM and mineralogy content and type, which gives it higher cation exchange capacity (Table 2) and specific surface area for REY-adsorption (Figure 2-B). Mineral type, CEC, and OM have been widely associated with REY-adsorption increases in soils (Fairhurst et al., 1995; Jones, 1997; Coppin et al., 2002; Shan et al., 2002; Pédrot et al., 2010; Tang and Johannesson, 2010a; Cidu et al., 2013). In contrast, kaolinitic and oxidic soils have low negative surface charge density, which gives them relatively low capacity of metal cation sorption (McBride, 1994). This explains the lower REY-adsorption values found for the Oxisol when compared with the Mollisol in this study.

Kinetic experiments for REY have reported increases in REY-adsorption in several soil types over time (Xiangke et al., 2000; Li, 2001; Coppin et al., 2002; Quinn et al., 2004; Tang and Johannesson, 2005; Davranche et al., 2005; Tang and Johannesson, 2010a), as it was observed for the Oxisol in the present study. In contrast, our data suggest that REY-adsorption and pH decreases over time for the Mollisol (Figure 3 C and D and table 2). These results indicate that there is surface competition and/or OH^- consumption or H^+ release. The main mineral phases for the Mollisol was 2:1 clays with aluminum (Al) in their structures, and significant differences in aluminum contents among REY-single treatments and Al^{3+} were observed for both studied reaction times. The observed results suggest that part of the Al present in solution for REY-single treatments may come from the mineral phase, especially muscovite. Similar results were reported by Coppin et al. (2002), who studied REY sorbed on clays similar to those found for the Mollisol in this study (muscovite and kaolinite) under different treatments. These authors attributed this fact to the dissolution of aluminum from clays. Thus, it is possible that clays weathered overtime, releasing Al^{3+} to solution, which consumed OH^-, decreasing pH and also competing with REY on the retention sites, reducing REY adsorption.

Europium was the REY with highest adsorption, especially in the Mollisol, irrespective of the reaction time and REY treatment. This is linked to the pH and, consequently, to Eu speciation in solution. The average for pH in solution for the Mollisol-Eu treatment was 6.72 while for Oxisol-Eu treatment was 4.42. According to the speciation model, the main species of Eu in solution was $Eu_2(OH)_2^{++++}$ for the Mollisol and Eu^{+++} for the Oxisol. $Eu_2(OH)_2^{++++}$ represented more than fifty percent of the expected europium species in solution, according to the speciation model fitted for the Mollisol-Eu treatment. Europium speciation has been studied in many studies under several experimental conditions (Wood, 1990; Millero, 1992; Spahiu and Bruno, 1995; Kang and Hahn, 2004; Luo and Byrne, 2007); however, only some recent studies report $Eu_2OH_2^{++++}$ in solution (Sun, Wang, et al., 2012; Sun, Chen, et al., 2012). According to Sun, Wang et al. (2012) studying europium sorption on graphene oxides nanosheets, the $Eu_2(OH)_2^{++++}$ species has attraction forces with anionic surface sites that easily result in the formation of metal-ligand complexes at pH > PZC. Further, cations of

greater valence have preference at soil adsorption sites (Sposito, 1989). This is a possible explanation for the higher adsorption of Eu in relation to other REY.

4.2.2-REY adsorbed in different pH values

Data reported in figure 6 and 7 show the influence of mineral phases and speciation from each soil on REY adsorption. The patterns of REY adsorption over the evaluated pH range in both soils are related to the developed electrical charge at each pH. Likewise, pH also controlled REY adsorption for both soils, with a more pronounced effect in the Oxisol. Several studies have reported the pH importance for REY adsorption (Fendorf and Fendorf, 1996; Jones, 1997; Aja, 1998; Cao et al., 2001; Tang and Johannesson, 2005; Bao and Zhao, 2008; Tang and Johannesson, 2010a). REY adsorption is further controlled by the nature of the clay minerals, as well as by the solution pH and the background electrolyte composition (ionic strength) (Laufer et al., 1984; Aja, 1998; Coppin et al., 2002; Wan and Liu, 2006). Taking into account the mineralogy of the studied Mollisol, 2:1 clays in this soil have high specific surface area, with a permanent negative surface charge due to the presence of the layered structures of aluminum octahedra and silicon tetrahedra sheets (Sposito, 1989), where isomorphic substitution of one cation (Si^{4+}) by another (Al^{3+}) with lower valence within these structures generates charge imbalances. This type of charge is independent of soil pH (Sposito, 1984), which explains the REY-adsorption pattern in the Mollisol above the pH of the estimated PZC, where REY adsorption values did not vary and pH dependent surface charge did not develop.

Adsorption increased at pH up to the PZC for the Mollisol. This is due to soil below its PZC having a positive charge, which repels metal cations. Clay PZC varies, e.g. kaolinite, which in average has a PZC between 3 and 4 (Kosmulski, 2009). Another variable could be the Fe and Al oxides present in this soil, where even at low concentrations (Table 2) these oxides can increase the PZC and thus contribute for the observed adsorption behavior. These factors may explain the REY-adsorption behavior on the Mollisol shown in figures 6 and 7 - B below the PZC, which contains kaolinite. It is also noticeable that the higher OM (Table 2) for Mollisol, which also may have some positively charged functional groups below this soil's PZC, is prone to character alteration and thus change the associated charge and soil PZC. Despite the high content of 2:1 clays in Mollisol, the OM may have a major role on REY adsorption below the PZC because it has been associated with increased metal adsorption even in temperate soils (Gerritse and Driel, 1984). Thus, it is possible that some organic compounds, which have overall PZC<4, together with silicated clays 1:1 were responsible for the increases in REY-adsorption with increasing pH up to the PZC estimated for this Mollisol. The reported PZC here was estimated (not determined by traditional methods); however, it is in agreement with the REY-adsorption plateau at a pH near the estimated PCZ. The REY adsorption for the Mollisol is a function of pH below the PZC of the soil even with the predominance of 2:1 clays.

The Oxisol REY-adsorption increased over the entire studied pH range. This trend is associated with its mineral-organic phase characterization (Figure 2-A and Table 2). It is well known that kaolinitic and oxidic soils are constituted by minerals having surface charges that depend on soil pH, known as variable or pH-dependent charges (McBride, 1994). Thus, the soil pH determines the predominance of negative or positive charges, and also the point at which the net surface charge is zero, the PZC. In addition, the role of OM is widely known to generate charge for Oxisols because the mineral phase in these soils is depleted in 2:1 clay minerals with structural negative surface charges. Several authors have reported REY-adsorption increases associated with higher OM and smaller clay contents (Shan et al., 2002; Pourret et al., 2007; Michaelides et al., 2010). Overall, it is difficult to measure the PZC of different OM components due to the complexity and diversity of organic compounds in the soil. Thus, it is possible that OM has contributed for REY-adsorption over all pH range, because various OM compounds could reach the PZC in different pH values (Kosmulski, 2009).

The REY adsorption trends for the Oxisol (Figure 7-A) may be separated according to the main mineral-organic influence at each highlighted pH range. The first increase (trend) in REY-adsorption, which indicates increases in negative surface charges, was probably due to silicate 1:1 clays and OM, which are the only soil components that could have PZC < 4.0. It also indicated that the PZC estimated for Oxisol in this study was appropriate for the first adsorption edge observed. Nevertheless, OM and silicate 1:1 clays (e.g., kaolinite) have been pointed as the main sources of negative charges in Brazilian Oxisols, especially below the overall PZC (Raij, 1973; Ker, 1997). When negatively-charged soil constituents increase, the negative surface charge in the soil is raised and the PZC is reduced (Gillman and Uehara 1980). Above the PZC, the next two REY-adsorption trends for the Oxisol (Figure 7-A – pH 4 through 7.8) may be associated with OM but are likely more influenced by oxide surfaces. Studies have reported the influence of oxides on REY adsorption, especially above pH 5.0 (Fendorf and Fendorf, 1996; Davranche et al., 2005). Piasecki and Sverjensky (2008) did a comprehensive study about REY sorption on different oxides under different conditions and observed differences in REY-adsorption between iron and aluminum oxides where hematite (Fe oxide) reached 100% REY sorption below pH 6.0, and alumina (Al oxide) REY 100% sorption was above pH 6.5. Based on these findings, it is proposed that the REY adsorption in the second trend (pH range from 4 through 6.2 – Figure 7-A) was due to the influence of hematite and/or goethite, while the third trend (pH range from 6.2 through 7.8 – Figure 7-A) was due to negative charge from gibbsite. At the highest pH, the REY-adsorption values may have been a mixture of precipitation and REY-adsorption onto oxides, because some REY were predicted to precipitate just below pH 7, especially for HREY(Fig. 6).

5 – Conclusion

The present study investigated the sorptive behavior of rare earth elements in soils of contrasting mineralogy and great representativeness Mollisol (US) and an Oxisol (Brazil). Our results have shown that clay mineralogy, which reflects the extent of weathering-leaching and the soil formation process, plays a major role in REY sorption, with the Mollisol being able to sorb almost twice as much REY as the Oxisol. However, as it happens with REY in other processes in the environment, it seems that their sorption trends follow the same behavior for each soil, irrespectively of the reaction time, especially in a competitive system were all REY coexist. Also, as commonly found in the literature, Eu was the most sorbed element hence it has the highest partioning coefficient (K_d). REY sorption is influenced by soil pH especially in the Oxisol, which is dominated by kaolinite and metal oxides, minerals with pH-dependent charge, as the main inorganic phases. Our findings are relevant and useful to predict REY accumulation in soils due to anthropogenic activities, which is of great importance especially in Brazil, where the use of phosphate fertilizers and phosphogypsum has been recently identified as a potential non-point source of REY to Brazilian agricultural soils.

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7 - References

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PAPER 3

Sorption and Buffer Capacity of Rare Earth Elements in Temperate and Tropical soils

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Abstract

Rare earth elements have been used extensively in modern societies, which might raise concerns about their fate in the environment. To better understand the adsorption behavior of rare earth elements (hereafter REY, including yttrium, Y) in tropical and temperate soils, sorption tests were performed adding all REY together and in the same molar concentration as they occur in the upper continental crust. For that, 0.3 g soils were weighed and suspended in a background solution with 30 mL of 5 mmoles L^{-1} $Ca(NO_3)_2$, with pH=6,0. Then all REY were added to reach the following concentration for the sum of REY ($\sum$REY): 0, 5, 10, 20, 40, 80, 160, 320, 800, 1600 and, 3200 μmol L^{-1}. The REY maximum sorption (MAC) and the binding intensity (KL) were evaluated using the Langmuir model, while the REY maximum buffering capacity (REY_{MBC}) was used as a parameter to predict REY susceptibility to change in the soil-solution interface. Results have demonstrated that cerium is the REY sorbed in higher amounts and that lutetium is the lowest sorbed REY, independently of the studied soil. The Langmuir model was efficiently used to fit adsorption data and estimate MAC and KL, except for sandier tropical soils. REY_{MBC} have demonstrated to be a great parameter to understand REY behavior on soils. Results for REY sorption varied among the distinct evaluated soil samples, and were linked to the physico-chemical properties of each soil. Considering that REY were recently termed as emerging contaminants, our findings are useful to predict REY behavior and fate in the environment, agroecosystems included.

Keywords: Rare earth elements, emerging contaminants, tropical soil, sorption, buffering capacity, REY-signature

1 –Introduction

Rare earth elements (REY) – Lanthanides + Y - have been introduced on soils in many ways and through different sources due to natural and/or anthropogenic processes (El-Ramady, 2008). They are classified as 17 chemical elements with atomic numbers between Z=57 and Z=71 more scandium (Sc, Z=21) and yttrium (Y, Z=39) (IUPAC, 2005). Despite their nomination, REY can be found in levels higher than some plant nutrients, e.g., there is almost the same amount of cerium and zinc in upper continental crust (Greenwood and Earnshaw, 1984).

As world population keeps growing, the use of phosphate fertilizers in agriculture is expected to increase due to the importance of phosphorus for plant nutrition and crop production, especially in Tropical agroecosystemns. Several studies have shown that phosphate fertilizers are the main 'non-point' source of REY to soils (Abdel-Haleem et al., 2001; Al-Thyabat and Zhang, 2015; Pang et al., 2002; Ramos et al., 2016a; Rutherford et al., 1994; Smidt et al., 2011; Turra et al., 2011; Waheed et al., 2011; Wen et al., 2001; Xu et al., 2002; Zhang et al., 2001; Zhang and Shan, 2001) and REY levels should keep growing in soils, since most phosphate fertilizers have REY in their composition (Ramos et al., 2016a). REY are considered neither essential nor toxic for the environment (El-Ramady, 2010). In fact, there is no common sense in the scientific community about the role of REY in living systems, agroecosystems included. Likewise, studies about ecological and human health risks involving REY are also limited (Ramos et al., 2016b).

Overall, soils are a major sink for solutes, including many organic and inorganic contaminants. As a consequence, they affect life as they might work also as a major pathway of heavy metals to the environment in terrestrial or aquatic systems (Kabata-Pendias, 2011). Several studies have pointed that soils are a major transfer media of REY to plants (Laul et al., 1979; Markert, 1987; Diatloff et al., 1996; Tyler and Olsson, 2002; Pang et al., 2002; Redling, 2006; Hu et al., 2006; Miao et al., 2008; Loell et al., 2011). As a result, soils are the main source of REY to the food chain. Therefore, studies aiming to understand adsorption reactions of REY on soils are relevant to predict their availability and mobility in the environment.

Many mathematical methods are used to fit adsorption data, with the Langmuir model being one of great utility for comparing solute retention in different soils, as it allows an estimate of the maximum adsorption capacity of the adsorbate (Sposito, 2008). Several studies have used the Langmuir model to understand REY sorption on different surfaces, such as on soils (Aja, 1998; Davranche et al., 2005; Gu et al., 2001; Kang and Hahn, 2004; Piasecki and Sverjensky, 2008b; Ridley et al., 2005; Wang and Liang, 2014; Yoon et al., 2002; Zhenghua et al., 2001).

Another interesting parameter to be investigated in studies involving the sorption of REY is the "buffering capacity". Such parameter was first introduced for studying phosphorus sorption by Holford and Mattingly (1976) and is related to the ability of the soil to resist against a change of the element's concentration in solution. Following that, a number of studies have started to use the "buffering capacity" of an element in the soil to predict its availability in agroecosystems, either in the

context of plant nutrition or for the purpose of environmental contamination (Holford and Mattingly, 1976; Joshi, Kremling, et al., 2006; Joshi, Seidel-Morgenstern, et al., 2006; Wisawapipat et al., 2009; Mejías et al., 2013; Shafqat and Pierzynski, 2014).

To date, studies regarding REY sorption on soil components have often evaluated this process under very specific conditions, such as adsorption in pure minerals (only one phase) or with only one REY, which is valuable, but limited to predict the real REY behavior in the environment. An extrapolation of the results from pure sorbents to heterogeneous natural systems is somewhat controversial due to the infinity of mineral/organic phases that are present in the whole soil. Thus, it is very important to study REY sorption on different soils, as they occur naturally in the environment.

It is well known that all REY tend to appear together and in certain molar ratios in the environment. Taking this into account, the present study aimed to evaluate REY sorption capacity using the Langmuir isotherm and the buffering capacity proposed by Holford and Mattingly (1976) in five contrasting soils. For that, we have applied all REY together, using a stock solution with the same specific molar ratio of the upper continental crust. Results provided by this study will be relevant for environmental regulations as well as to a better understand of the fate of REY in the soil-plant system.

2 - Material and Methods
Sampling

Five soils were collected at the 0-20-cm depth in areas of native vegetation, four of them in Brazil and one in the USA. All sites had no records of anthropic intervention. Sampling from the USA (hereafter called soil A) was performed in the Critical Zone Observatory in zero order basin of the La Jara catchment, National Preserve (New Mexico-United States) (Figure 1-A). Sampling from Brazil were performed in three native areas in farms located in three different states of the country, which represents the main agriculture ecosystem in Brazil. The three states are| Mato Grosso (hereafter called soil C), Goiás (hereafter called soil D), and Minas Gerais (hereafter called soils B and E) (Figure 1-B). The composite samples were air-dried and passed through a 2-mm sieve for further analysis at the Arizona Laboratory for Emergent Contaminants (ALEC).
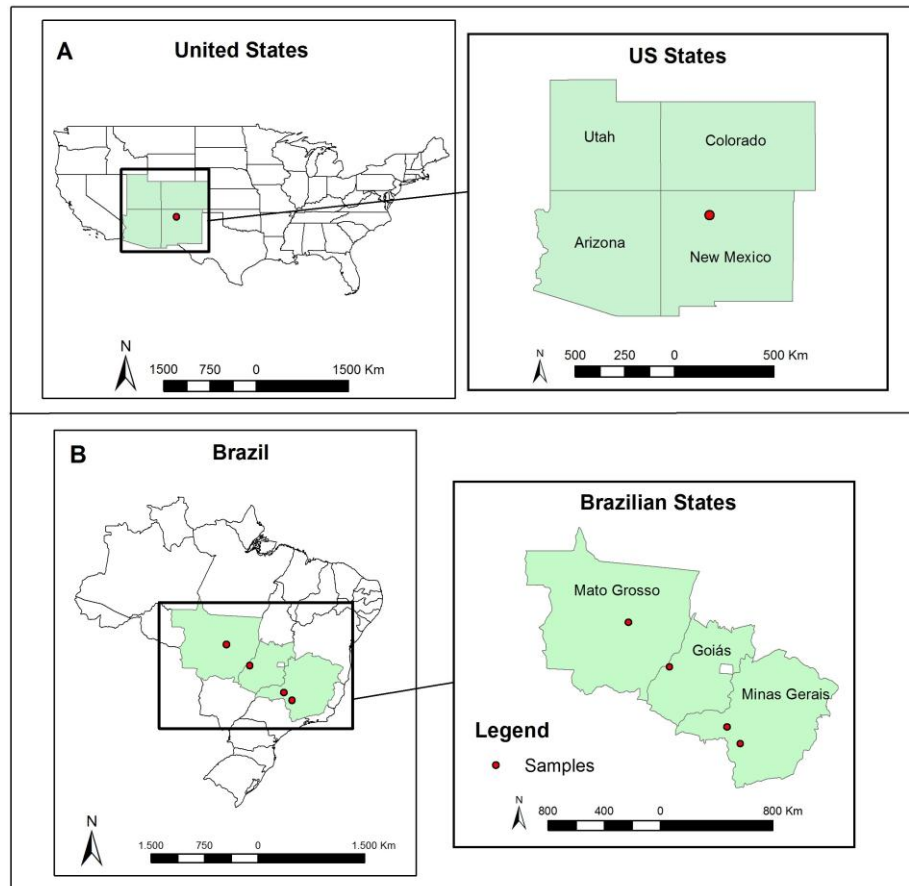
Figure 1: location of the sampling sites in USA (A) and Brazil (B). "Soil A" site: Valles Caldera National Preserver, New Mexico – USA; "Soil B" site: São Roque de Minas, Minas Gerais – Brazil; "Soil C" site: Água Limpa farm, Mato Grosso – Brazil; "Soil D" site: Aragarças, Goiás – Brazil; "Soil E" site: Santa Juliana, Minas Gerais – Brazil.

Soil Characterization

X-Ray Diffraction

For all five samples, the mineral phases were evaluated by X-ray diffraction using synchrotron light source (Stanford Synchrotron Radiation Light source-SSRL, Stanford-CA). For that, samples were dispersed on adhesive tape and the XRD patterns were calibrated with a LaB_6 standard and converted to wavelength using non-linear curve fit and the Bragg equation. Mineral identification was performed using the Philip's X'pert High Score Plus program version 2.2a (2.2.1) and also with the aid of the webminerals (webmineral.com, 2016) databases.

Physical and Chemical Analysis

The particle size distribution was determined according to Vettori, L. (1969) for all soils from Brazil, while percentage of size-class fractions in the soil from the USA were determined using ASTM C 1070–01 test (ASTM, 2000).

All soil samples were air-dried and grounded to pass through a 100-mesh nylon sieve. The samples were digested by means of an alkaline fusion method. Aliquots of 0.05±0.0001g from each sample were fused with 1.5±0.0001g of flux (lithium metaborate-tetraborate) in platinum crucibles at 1000°C in a fusion machine (Katanax, SPEX Sample Prep, Metuchen-NJ). After cooling, the resulting bead was dissolved in beakers containing 50 mL of solution of 10% HNO_3. Each beaker was transferred to a hot plate at 120 ± 20°C with magnetic stirring for complete solubilization. After that, the samples were diluted in a 2% solution of HNO_3. Certified reference materials (OREAS Research exploration® 100, 100a, and 100b) and blank samples were included for quality control to the analytical series.

Element contents in the digested solutions were determined by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent, 7700x with an Agilent ASX 500 autosampler). The oxides were calculated from conversion numbers using concentration obtained from ICP-MS and their respective elementary formula (molar ratio). The REY concentrations in all standard reference materials used in this study are shown in Table 1. According to this table, the recoveries for all REY were considered satisfactory, which supports that our QA/QC protocols were adequate as to guarantee data accuracy for REY analyses. High temperature oxidation followed by infrared detection of CO_2 was used to determine the total organic carbon.

Cation exchange capacity capacity (CEC = $\sum$ Ca^{2+}, Mg^{2+}, K^+, Na^+, H^+, Al^{3+}) and ΔpH were calculated according to the method described in Vettori, L. (1969). The point of zero charge (PZC) was estimated by PZC = 2 pH KCl – pH H_2O (pH KCL = 1:25, v/v, solution 1 mol.L^{-1} KCl / soil; pH H_2O = 1:25, v/v water/soil) according to Keng and Uehara (1973).

Table 1: REY certified and determined concentrations, and recoveries found for certified reference materials of the OREAS Research exploration® 100, 100a, and 100b.

REY	Certified value (mg kg^{-1})			Obtained value (mg kg^{-1})			Mean recovery (%)		
	*	**	***	*	**	***	*	**	***
La	260	816	789	230	842	739	89	103	94
Ce	463	1396	1331	412	1437	1262	89	103	95
Pr	47.1	134	127	42.1	135.9	118.4	89	101	93
Nd	152	403	378	123	368	323	81	92	86
Sm	23.6	48.8	48	21.7	52.1	45.5	92	107	95
Eu	3.7	8.1	7.8	3.3	8.5	7.4	90	105	95
Gd	20.3	42	40	18.8	35.3	31.2	93	84	78
Tb	3.8	5.9	5.4	2.9	4.1	3.6	75	69	67
Dy	23.2	33.3	32.1	21.1	34.0	30.3	91	102	94
Ho	4.8	6.5	6.3	4.6	6.9	6.2	95	106	98
Er	14.9	19.5	18.7	14.1	20.4	18.4	94	104	98
Tm	2.3	2.9	2.7	2.1	3.0	2.7	93	103	101
Yb	14.9	17.5	17.6	14.0	19.2	17.3	94	110	98
Lu	2.3	2.7	2.6	2.1	2.7	2.5	92	103	97
Y	95.5	135	133	121	178	160	127	132	120

*, **, and *** are certified reference materials OREAS Research exploration® 100, 100a, and 100b, respectively.

REY Adsorption

Stock and Background Solutions

REY adsorption experiments were conducted trying to simulate the conditions that REY are found in the environment, i.e., always together. In this context, 5 μmol L^{-1} of $Ca(NO_3)_2$ (pH = 5.5, ionic strength 15 mmol L^{-1}, room temperature) was used as a background solution. Besides, stock solutions with all rare earth elements were prepared. The concentration for each element in the stock solution was calculated according to the REY molar ratio previously found for upper continental crust by Taylor and Mclennan (1995). Stock solutions were prepared following the molar ratio 1 : 2.11 : 0.23 : 0.83 : 0.13 :0.02 : 0.11 : 0.01 : 0.09 : 0.02 : 0.06 : 0.009 : 0.05 : 0.008 : 1.14 for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and, Y respectively. The stock solution final concentration for each REY was 679.5, 1437.1, 158.5, 567.1, 94.2, 18.2, 76.0, 12.7, 67.8, 15.3, 43.3, 6.1, 40.0, 5.8, 778.5 μmol L^{-1} for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and, Y, respectively. Thus, final concentration for the sum of all REY (∑REY) was 4000 μmol L^{-1}. REY certified standards

were used to prepare all REY solutions (stock solution) together with the background solution. The pH of the stock solution was adjusted to 6.0±0.1 with 15 μmol L^{-1} HNO$_3$ and 5 μmol L^{-1} Ca(OH)$_2$ (ionic strength = 15 mmol L^{-1}). For the adsorption experiment, the ∑REY was used as the parameter to calculate all fourteen doses used to evaluate the REY maximum adsorption and buffering capacity in the soils.

Batch Test

All soils were air-dried and grounded in agate mortar. Next, 0.3 g were weighed and suspended with 30 mL of background solution. Before adding the REY in the tubes, the pH was adjusted to 6.0±0.1 using either 15 μmol L^{-1} HNO$_3$ or 5 μmol L^{-1} Ca(OH)$_2$ (ionic strength = 15 mmol L^{-1}). After two weeks of pH adjustment, all REY were added from the stock solution in specific volumes to reach the specific ∑REY concentrations, which were considered the initial concentrations for the adsorption reactions (time 0h). The proposed increasing ∑REY concentrations were 0, 5, 10, 20, 40, 80, 160, 320, 800, 1600, and 3200 μmol L^{-1}. Suspensions were left shaking for 72-h, with alternate cycles of 12 h of shaking and 12 h of resting and then, centrifuged for 10 min at 14,000 rpm and finally filtered (0.45 μm). Blank tests were performed during this study to determine possible contamination in the analysis and also possible REY-desorption from the soils. After the time-reaction, REY contents in the equilibrium concentration were determined by inductively coupled plasma mass spectrometry (ICP-MS). Calibration standards for each REY were prepared matching the matrix composition with samples diluted for ICP-MS analysis in order to account for matrix interferences. The detection limits in ng L^{-1} for Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were 0.1, 0.4, 0.02, 0.4, 0.7, 0.1, 0.6, 0.1, 0.1, 0.1, 0.1, 0.1, 3.7, and 10.2, respectively. Figure 2 shows the organogram of the test, where it can be seen the molar ratio, the sum of REY, and the individual concentration for all assessed REY doses.

Figure 2: Organogram of the batch test experiment.

REY Maximum adsorption and buffering capacity – MAC and MBC

The REY concentrations were calculated using weight as unit. Equation 1 was used to calculate REY adsorbed per unit weight of adsorbent:

Eq.(1): $Q = \dfrac{((Ci - (Ce - Ce\sum REY - Ce - \sum REY - 0)) * Vsol.}{Msoil}$

where, Q is the REY adsorbed (mg kg^{-1}); Ci and Ce are the initial and the equilibrium ∑REY concentrations in the solution (mg L^{-1}), respectively; Ce$_{\sum REY-0}$ is the equilibrium REY concentration obtained from the soil (desorption in mg L^{-1}); V is the volume of the solution (mL); and M is the mass of the adsorbent (g). The batch methodology used in this work has been documented in several studies involving metal adsorption and desorption. Additional details are given in USEPA (1999).

Adsorption data for each REY were fitted to the Langmuir isotherm in order to estimate the REY maximum adsorption capacity (REY$_{MAC}$) and REY maximum buffering capacity (REY$_{MBC}$), according to Holford and Mattingly (1976). The Langmuir isotherm (Eq. 2) has been used in several studies concerning metals adsorption on soils, and its linearized form is presented in Eq. (3), as follows:

Eq. (2): $q = \dfrac{KL * REYMAC * Ceq}{1(+KL * Ceq)}$

| Soil A | Soil B | Soil C | Soil D | Soil E |

Experimental Concentrations
- Background Solution - 5 mmol L^{-1} Ca(NO$_3$)$_2$
- Volume - 30 mL
- 0.3 g of Soil
- Initial pH = 6.0±0.1
- Reaction time - 72 hours

Triplicate

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
REY															
Molar Ratio															
Treatments	1	2,14	0,23	0,83	0,13	0,02	0,11	0,01	0,09	0,02	0,06	0,01	0,05	0,01	1,14
∑REY (µM)	**Individual Initial Concentration (µM)**														
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
5	0.85	1.80	0.20	0.71	0.12	0.02	0.10	0.02	0.08	0.02	0.05	0.01	0.05	0.01	0.97
10	1.70	3.59	0.40	1.42	0.24	0.05	0.19	0.03	0.17	0.04	0.11	0.02	0.10	0.01	1.95
20	3.40	7.19	0.79	2.84	0.47	0.09	0.38	0.06	0.34	0.08	0.22	0.03	0.20	0.03	3.89
40	6.79	14.37	1.59	5.67	0.94	0.18	0.76	0.13	0.68	0.15	0.43	0.06	0.40	0.06	7.79
80	13.59	28.74	3.17	11.34	1.88	0.36	1.52	0.25	1.36	0.31	0.87	0.12	0.80	0.12	15.57
160	27.18	57.48	6.34	22.68	3.77	0.73	3.04	0.51	2.71	0.61	1.73	0.25	1.60	0.23	31.14
320	54.36	114.9	12.68	45.37	7.53	1.46	6.08	1.01	5.42	1.22	3.46	0.49	3.20	0.46	62.28
800	135.9	287.4	31.71	113.4	18.83	3.64	15.21	2.53	13.55	3.05	8.65	1.23	8.00	1.15	155.7
1600	271.8	574.8	63.41	226.8	37.66	7.29	30.41	5.07	27.11	6.10	17.31	2.46	16.00	2.30	311.4
3200	543.6	1149.	126.8	453.6	75.3	14.5	60.8	10.1	54.2	12.2	34.6	4.9	32.0	4.6	622.8

Eq. (3): $\dfrac{Ceq}{x} = \dfrac{1}{KL*REYMAC} + \dfrac{Ceq}{REYMAC}$

where, q is the REY adsorbed (mg kg^{-1}), KL is the REY sorption strength (L mg^{-1}), REY$_{MAC}$ is the maximum REY adsorption capacity (mg kg^{-1}), Ceq is the equilibrium REY concentration (mg L^{-1}) and X is the amount of REY sorbed (mg kg^{-1}), Xm. Besides, the maximum buffering capacity (MBC) was calculated as the maximum slope of the Langmuir equation founded at C = 0 (Holford and Mattingly, 1976), as follows in equation 4:

Eq. (4): $REYMBC = KL * REYMAC$

The parameters of the Langmuir isotherm were estimated by the "sums of square" methods using Microsoft Excel Solver$^{®}$. Furthermore, to assess the variability in the fitted model, a nonparametric bootstrap (Efron and Tibshirani, 1994) was performed by repeatedly sampling (1,000 bootstrap replications) from the original data to get a better approximation of confidence intervals.

3 –Results and Discussion

Soil Physical and Chemical characterization

The physico-chemical properties of the studied soils are shown in Table 2. Among the tropical soils (Soils, B, C, D and, E), soils B and E present higher amounts of iron and aluminum oxides, whereas soils C and D have greater amounts of silicon oxide. Soil E has showed also a great content of titanium oxide. All of these results are in agreement with data concerning soil textures. Soils B and E are clayey soils, while soils C and D are sandier ones. It is well known that iron and aluminum oxides are commonly found in the clay fraction of tropical soils. Silicon oxide is frequently present in sandy soils as quartz, which has no effect in the soil physico-chemical characteristics (Kampf and Curi, 2003). Other soil features are in agreement with these results found for soil texture. Soils B and E have the highest cation exchange capacity (CEC) and also the greatest organic matter content. For weathered soils, it is common to associate texture with CEC, as the amount of clay minerals, in any texture fraction, is very low and the charge generation depends mainly of the clay-size and the pH of the soil. For tropical soils, the main source of negative net charge is organic matter (Lopes and Guilherme, 2016), which help us to predict CEC and sorption values.

Differently from what was previously discussed for tropical soils, there is no association between CEC and texture for soil A, i.e., this soil has the lowest clay content and the highest CEC among all soils. Also, potassium and sodium oxides are present in high levels in soil A, 2.66 and 2.1%, respectively. These results are understandable, since this soil was formed under temperate conditions, allowing elements such as potassium and sodium to remain in clay minerals. Also, this soil's clay minerals have a high specific surface area (SSA), which confers it a high negative net charge (Staff,

2010). This fact also explains the low level of Fe and Al oxides in soil A. All of these soil features will help us understand REY sorption data showed ahead.

Table 2. Chemical and physical characteristics of soils.

	Unit	Soil				
		Soil A	Soil B	Soil C	Soil D	Soil E
O.C.	%	14	2.2	1.2	1.8	3.4
pH_{H2O}		6.85	4.35	4.80	5.10	5.10
pH_{KCl}		5.20	4.25	4.70	4.90	4.50
PZC		3.55	4.15	4.60	4.70	3.90
CEC	$cmol_c\ dm^{-3}$	19.7	10.2	4.8	6.2	11.5
Oxides SiO_2		51.8±3	18.3±0.5	76.9±6	63.1±1	17.3±6.3
Al_2O_3		8.1±0.5	34.6±0.9	7.1±0.7	4.9±0.2	38.8±0.7
Fe_2O_3		1.38±0.1	14.1±0.4	3.4±0.2	1.3±0.1	10.2±0.2
TiO_2	%	0.48±0.1	1.5±0.2	0.6±0.01	0.2±0.01	4.4±0.01
MnO		0.07±±0.1	0.02±±0.1	0.01±0.1	0.003±0.1	0.03±0.1
K_2O		2.66±0.1	0.4±0.1	-	-	1.1±0.1
Na_2O		2.1±0.2	0.5±0.1	0.6±0.1	-	-
La		22.5±1.5	3.27±0.9	3.3±0.2	9.4±1	51±2
Ce		42.1±2.9	106.1±9.2	5.8±0.7	26.9±3	165.3±3
Pr		4.7±0.3	0.89±0.2	0.5±0.04	2.3±0.2	11.4±0.2
Nd		14.8±1.3	3.19±0.9	1.4±0.07	7.5±0.7	36.6±0.8
Sm		3±0.2	1.15±0.3	0.4±0.006	1.6±0.2	6.8±0.2
Eu		0.6±0.1	0.38±0.1	0.1±0.002	0.4±0.01	1.6±0.03
Gd		2±0.1	2.52±0.5	0.4±0.04	1.4±0.1	5.3±0.1
REY Tb	$mg\ kg^{-1}$	0.4±0.1	0.48±0.1	0.1±0.003	0.2±0.02	0.8±0.02
Dy		2.7±0.1	4.60±1.2	0.6±0.05	1.7±0.1	6.1±0.1
Ho		0.6±0.1	1.06±0.3	0.2±0.01	0.4±0.02	1.3±0.02
Er		1.8±0.1	3.29±0.8	0.6±0.07	1.3±0.1	4.1±0.07
Tm		0.3±0.1	0.54±0.1	0.1±0.01	0.2±0.01	0.6±0.01
Yb		1.9±0.1	3.39±0.8	0.7±0.05	1.6±0.06	4.5±0.1
Lu		0.4±0.1	0.55±0.1	0.1±0.01	0.3±0.01	0.7±0.01
Y		14.4±0.1	27.3±6	3.7±0.3	8.4±0.6	28.5±0.6
∑REY		112.2	158.7	18.1	63.6	324.6
Texture Sand		46	3	75	71	12
Silt	%	38	15	5	4	15
Clay		16	82	20	25	73

pH_{H2O} - 1:2.5 soil:water - v/v (natural pH); n=5
pH_{KCl} - 1:2.5 soil:1M KCl - v/v, n=5
PZC = 2 pH_{KCl} - pH_{H2O};
Error bars for oxides and REY were from n=2

Total concentrations of REY are also shown in table 2. The total levels of REY varied among the tropical soils, which is in agreement with the data found by Sá Paye et al. (2016), who have found different REY levels for distinct tropical soils in Brazil. Also, REY total contents present in soil A corroborate those found by Vázquez-Ortega et al. (2016) in similar soils of the USA. The natural pH value found for all soils are also in agreement with literature values in both cases, i.e., for temperate and tropical soils. The point of zero charge (PZC) showed interesting differences among the soils, with the lowest value found for soil A. Knowing the mineralogical phases of each soil, it is possible to establish a relationship between soil mineralogical and chemical characteristics, such as PZC, CEC,

and element concentration, which in turn interferes directly in the generation of the soil net charge and, consequently, in the sorption of REY. Among all soils, soil A has shown the lower PZC probably due to its mineralogy (presence of 2:1 clays) and also the higher organic matter concentration (table 2). Nevertheless, for the Brazilian soils, the PZC calculated for soil E was the lowest among all of them. It may be due to the characteristics of its colloidal fraction, such as organic matter, kaolinite and oxide amounts. Soil chemical characteristics are a direct result of the soil mineral phases, especially for tropical soils, which have oxides and 1:1 clays as the main mineral phases. It is well known that these minerals are pH-dependent (McBride, 1994) and that this variation can change soil chemical characteristics such as, net charge, which will interfere directly in REY sorption.

Soil Mineralogical Characterization

The XRD analyses for all soils are shown in figure 3, with diffractograms recorded in the whole soil samples, including silt and sand. Soil A presents as crystalline mineralogical phases, the following minerals: albite, anorthite, augite, kaolinite, illite, orthoclase, and quartz. All minerals that were found in soil A are commonly found in temperate soils, as observed by Vasques-Ortega et al. (2015). It is well known that 2:1 clays have high negative charge density due to isomorphic substitution in these minerals. Such negative charges, coming from isomorphic substitution, are permanent and cannot be changed with the pH, i.e., they affect soil sorption and buffering capacity processes irrespectively of pH changes.

In contrast, for the studied tropical soils, there are only a few peaks of 2:1 clay minerals, with mica and Al-hydroxy interlayer vermiculite being found for all soils. Several authors have reported the presence of HIV minerals in acid soils (Almeida et al., 2000; Curi et al., 1984; Kampf and Klant, 1977; Lepsch and Buol, 1974; Marques et al., 2002). In tropical soils, HIV occurs mainly at the clay fraction on the top-soil (Almeida et al., 2000; Curi et al., 1984; Demattê and Holowaychuck, 1977; Kampf and Klant, 1977; Lepsch and Buol, 1974) and alongside organic matter is a great source of negative charge.

Although mica was observed in the tropical soils, it is impossible to determine its exact type. However, since all soils were collected under the "Cerrado" biome, it is plausible that it may be muscovite, because biotite occurs only in less-weathered soils (Luz et al., 1992). Independently of that, mica is not an expansive clay and it has lower contribution to negative charge, when compared with HIV minerals (Reid-Soukup and Ulery, 2002). According to figure 3, soil E has shown the highest intensity peaks for HIV and mica-like minerals among the tropical soils, followed by soils B, D, and C, respectively. HIV and mica are the only minerals in the tropical soils that have no pH-dependent charge. All other minerals are pH-dependent, such as 1:1 clay, oxides or tectosilicates, as follows: anatase, goethite, hematite, kaolinite, and quartz (present in all tropical soil), ilmenite (present in soils C, D and, E), gibbsite (present in soils B and E), and magnetite (present only in soil E). Overall, the adsorption of REY and the buffering capacity of the soils are directly linked with soil mineralogical characteristics. Thus, with the predominance of low activity components in the clay fraction (i.e.,

lower net negative charge), the tropical soils are expected to have less affinity for REY, which are all presented in the cationic form at the normal pH range of soils.
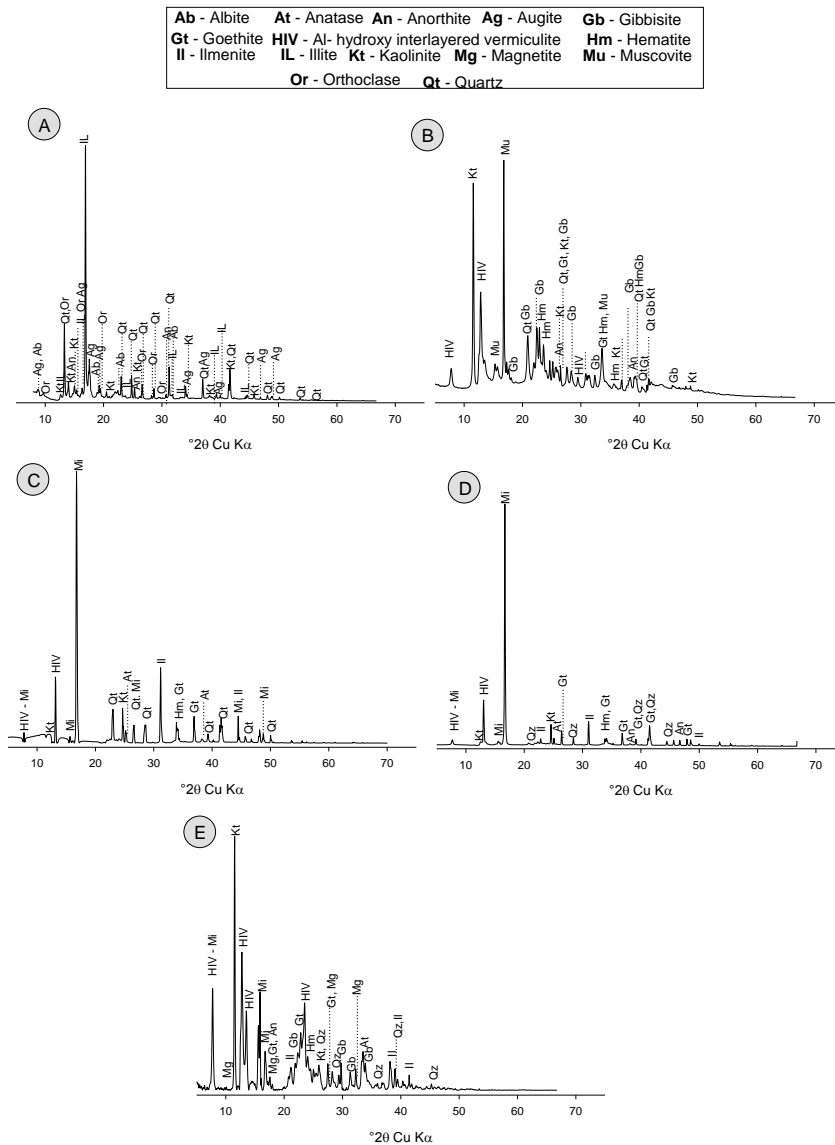

Figure 3: X-ray diffractograms for all soils. Soil A - Albite (NaAlSi$_3$O$_8$), Anorthite ((Ca,Na)(Al,Si)$_4$O$_8$,) Augite (Ca(Mg, Fe, Al)(Si,Al)$_2$O$_6$), Kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), Illite (K,H$_3$O)(Al,Mg,Fe)$_2$(Si,Al)$_4$O$_{10}$[(OH)$_2$,(H$_2$O)], Orthoclase (KAlSi$_3$O$_8$) and, Quartz (SiO$_2$). Soil B - Anatase (TiO$_2$),Al-Hydroxy interlayed Vermiculite (Mg;Fe$_3$;Al)$_3$(Si; Al)$_4$O$_{10}$(OH)$_{24}$H$_2$O, Gibbsite (Al(OH)$_3$), Goethite (Fe$_3$OOH), Hematite (Fe$_2$O$_3$), Kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), Muscovite KAl$_2$(Si$_3$Al)O$_{10}$(OH,F)$_2$) and, Quartz (SiO$_2$). Soil C - Anatase (TiO$_2$), Al-Hydroxy interlayed Vermiculite (Mg;Fe$_3$;Al)$_3$(Si; Al)$_4$O$_{10}$(OH)$_{24}$H$_2$O, Ilmenite (FeTiO$_3$), Kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), Mica (i.e. Muscovite KAl$_2$(Si$_3$Al)O$_{10}$(OH,F)$_2$) and Quartz (SiO$_2$). Soil D - Anatase (TiO$_2$), Al-Hydroxy interlayed Vermiculite (Mg;Fe$_3$;Al)$_3$(Si; Al)$_4$O$_{10}$(OH)$_{24}$H$_2$O, Gibbsite (Al(OH)$_3$), Goethite (Fe$_3$OOH), Hematite (Fe$_2$O$_3$), Ilmenite (FeTiO$_3$), Kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$), Mica (i.e. Muscovite KAl$_2$(Si$_3$Al)O$_{10}$(OH,F)$_2$),

Magnetite (Fe_3O_4) and Quartz (SiO_2). Soil E - Anatase (TiO_2), Al-Hydroxy interlayed Vermiculite ($(Mg;Fe_3;Al)_3(Si; Al)_4O10(OH)_{24}H_2O$), Gibbsite ($Al(OH)_3$), Goethite ($Fe_3OOH$), Hematite ($Fe_2O_3$), Ilmenite ($FeTiO_3$), Kaolinite ($Al_2Si_2O_5(OH)_4$), Mica (i.e. Muscovite $KAl_2(Si_3Al)O_{10}(OH,F)_2$) and Quartz ($SiO_2$).

Soil REY Sorption and Buffer Capacity.

Tropical x Temperate Soils

The KL and REY_{MAC} parameters of the Langmuir isotherm, as well as the REY_{MBC} are shown in table 3. In order to compare temperate and tropical soils, soil E was chosen due to its high values found for REY_{MAC} and REY_{MBC}. Among all REY, cerium had the highest maximum adsorption with 1837 and 3641mg kg^{-1} for soil A and E, respectively. Overall, soil A has higher values for REY_{MBC}, while soil E has greater values for REY_{MAC}. Yet, it seems that soil A is capable to retain REY easily, as it has demonstrated higher sorption strength (KL) for all REY.

As mentioned before, soil A was formed under temperate conditions, having 2:1 clays as the main mineral phases. Such minerals have high specific surface area (SSA) and permanent charge (McBride, 1994). Because of that, we expected higher REY_{MBC} and REY_{MAC} values for soil A, when compared with the other soils. However, only the REY_{MBC} was higher for soil A, with REY_{MAC} being greater for soil E, among all soils. This fact may be associated with soil texture, since soil A has lower clay percentage compared with soil E.

The HIV's - minerals that have also a great SSA - certainly have contributed for the REY_{MAC} values found for soil E, which seems to be present a significant amount of such mineral. In fact, the broader peak found for HIV in this soil is an additional evidence that the SSA of HIV in this soil is greater than in any other soil (Figure 3 - E). To illustrate the role of the HIV minerals for REY sorption on soils, several works in the literature have reported metal adsorption in the interlayers of the HIV (Barnhisel and Bertsch, 1989; Maes et al., 1999; Saha et al., 2001). In spite of this, the REY_{MAC} value found for soil A was higher than those verified for the other tropical soils, even for soil B, which has a greater clay percentage than soil A. This indicates that even though clay content is important, clay type (i.e., mineralogy) has a major effect in REY adsorption on soils (Bradbury and Baeyens, 2002; Bruque et al., 1980; Coppin et al., 2002; Olivera Pastor et al., 1988).

In general, the REY_{MBC} values found for soil A were at least ten times higher than those found for all tropical soils, which is related to the mineralogy and the organic matter content of soil A. Soil A has also the highest KL values for each REY, which indicates that this soils is less susceptible to changes in REY concentration in solution. In this context, soil A would be better for preventing REY contamination than the others soils due to its REY_{MBC} values, in the event of REY becoming a hazard to agroecosystems. These results suggest also that buffering capacity does not increase upon increasing clay percentage. Thus, considering that REY behavior in the environment is still a matter of debate, it

is important to observe, besides soil maximum adsorption, the KL and buffering capacity, which might provide additional information for a better evaluation of REY sorption/availability in the environment.

Tropical Soils

Among the tropical soils, soil E has the highest values for REY_{MAC} and REY_{MBC}, for all REY. Cerium was the REY with greatest adsorption, having the highest maximum adsorption for all soils, being 3641, 2687, 1953, and 1869 mg kg^{-1} for soil E, D, C, and B respectively. On the other hand, it seems that ytterbium is the less changeable REY in the soil/solution system, as its values for REY_{MBC} were the highest among all REY, as follows: 90.4, 61.2, 43.7, and 20.4 mg kg^{-1} for soil E, D, B, and C, respectively.

These results are related to soil's E mineral phase composition, oxide contents, organic matter amounts, texture, and PZC. It is well known that quality and amount of the mineral phases and organic matter affect directly the PZC of the whole soil (Appel et al., 2003; Gillman and Uehara, 1980; Keng and Uehara, 1973). Soil E has 5.8% of organic carbon, which is the highest value among all tropical soils. The PZC of organic matter is usually low, being lower than 4.0 (Ghosh et al., 2008; Kosmulski, 2009; Sheng et al., 2009; Wijting et al., 2008). As a result, at pH 6.0 (tested in this study) organic matter certainly is the main source of negative charges. Lopes and Guilherme (2016) have mentioned the importance of organic matter to increase the CEC and adsorption of cationic elements in tropical soils. Also, several authors have demonstrated increases of REY sorption associated with higher organic matter contents (Michaelides et al., 2010; Pourret et al., 2007; Shan et al., 2002).

Besides the role of organic matter, the results found for soil E could also be associated with the type and amounts of oxides and kaolinite found in this soil. As demonstrated here and elsewhere, tropical soils have kaolinite and oxides as the main mineral phases (Kampf and Curi, 2003; Resende et al., 2011). These minerals are linked with REY adsorption, especially above pH 5.0 (Davranche et al., 2005; Fendorf and Fendorf, 1996). Among all tropical soils, soil E has showed a greater diversity of oxide types and the highest peak intensity for kaolinite in the mineral phases. Furthermore, it also has a high peak intensity for HIV (Figure 3) and the highest value of titanium oxides (4.4%, Table 2), which corroborate with values found elsewhere for tropical soils (Ker, 1997).

It is understandable the discrepancy for REY_{MAC} and REY_{MBC} values found between soil E and soils C and D, as not only the texture, but also kaolinite peak intensity and organic matter are extremely different. These parameters have been pointed out as the main sources of negative charges in Brazilian Oxisols, especially below the overall soil´s PZC (Ker, 1997; Raij, 1973). Nevertheless, for the comparison between soil B and soil E, only kaolinite and organic matter are not able to explain the great differences in adsorption and buffer capacity. In this case, it is also worth to mention the PZC, which is lower for soil E. Thus, in addition to the features already mentioned, it is possible that the titanium oxides (alongside organic matter), expressed as anatase and ilmenite (and others not detected) (figure 3-E), have contributed to decrease PZC, hence increasing the REY_{MAC} and REY_{MBC}, taking into

account the pH of 6.0. In an extensive review, Kosmulski (2009) has demonstrated that the PZC for titanium oxides is lower than those commonly found for iron and aluminum oxides. Moreover, Piasecki and Sverjensky (2008a), studying REY adsorption in a great pH range on different oxides (e.g., iron, aluminum, silicon, and titanium) have shown that REY adsorption on titanium oxides reached 100% quickly (around pH 5.5), when compared with the other oxides. Thus, considering similar texture, organic matter content, and the same pH conditions, titanium oxides found in soil E certainly contributed for the REY_{MAC} and REY_{MBC} values, although the explanation for this relationship is still unclear (Wisawapipat et al., 2009).

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Table 3. Langmuir isotherm parameters (KL, REY_{MAC}) as well as the REY_{MBC}

	Soil A			Soil B			Soil C			Soil D			Soil E		
	KL^*	REY_{MAC}	REY_{MBC}	KL	REY_{MAC}	REY_{MBC}	KL	REY_{MAC}	REY_{MBC}	KL	REY_{MAC}	REY_{MBC}	KL	REY_{MAC}	REY_{MBC}
	$L\,mg^{-1}$	$mg\,kg^{-1}$	$L\,kg^{-1}$	$L\,mg^{-1}$	$mg\,kg^{-1}$	$L\,kg^{-1}$	$L\,mg^{-1}$	$mg\,kg^{-1}$	$L\,kg^{-1}$	$L\,mg^{-1}$	$mg\,kg^{-1}$	$L\,kg^{-1}$	$L\,mg^{-1}$	$mg\,kg^{-1}$	$L\,kg^{-1}$
La	0.706	701.1	495.3	0.027	674.17	18.1	0.005	1105.2	5.4	0.009	930.5	8.6	0.021	1564.3	32.7
Ce	0.196	1837.4	360.8	0.010	1869.77	19.3	0.002	2687.9	6.5	0.009	1953.0	16.7	0.011	3641.5	40.2
Pr	1.893	224.5	424.9	0.102	232.34	23.8	0.028	277.2	7.9	0.069	251.0	17.3	0.110	444.9	49.0
Nd	0.389	876.7	340.9	0.035	858.48	29.9	0.007	1166.7	8.7	0.023	976.2	22.2	0.034	1607.7	54.4
Sm	2.054	172.6	354.5	0.127	206.05	26.1	0.049	214.5	10.5	0.164	178.8	29.4	0.208	322.4	67.1
Eu	11.859	32.7	388.2	0.725	38.57	28.0	0.240	42.8	10.3	0.850	35.6	30.2	1.233	63.0	77.6
Gd	3.629	127.5	462.9	0.141	160.82	22.6	0.070	154.6	10.8	0.240	112.1	27.0	0.238	255.3	60.7
Tb	31.557	20.5	646.6	0.621	28.56	17.7	0.278	26.7	7.4	1.073	21.5	23.1	1.410	50.5	71.2
Dy	1.738	129.0	224.2	0.082	213.03	17.5	0.066	163.6	10.8	0.233	134.9	31.5	0.270	258.3	69.8
Ho	7.392	31.9	235.9	0.489	50.23	24.6	0.258	47.5	12.3	0.927	37.5	34.7	1.137	60.6	68.9
Er	2.168	97.5	211.5	0.199	150.86	30.1	0.100	137.7	13.8	0.308	117.5	36.2	0.416	182.7	76.0
Tm	0.832	39.9	33.2	0.744	43.42	32.3	0.353	47.6	16.8	1.606	20.8	33.4	2.801	27.1	76.1
Yb	0.189	159.6	30.1	0.274	159.26	43.7	0.153	133.6	20.4	0.528	116.0	61.2	0.486	185.9	90.4
Lu	1.456	23.2	33.8	0.953	27.17	25.9	0.367	28.3	10.4	2.015	17.4	35.1	3.080	29.2	89.9
Y	0.701	520.0	364.6	0.023	590.02	13.4	0.006	714.8	4.0	0.010	733.6	7.6	0.026	1161.0	29.7

REY Adsorption Behavior by the Langmuir Model

Experimental data for all REY sorption as well as curves estimated by the Langmuir equation are shown in figure 4. Each point in the figures represents the mean from three replicates. The values over each graphic represent the 5th and 95th percentile of bootstrap replications of the REY_{MAC}, KL, and REY_{MBC} data set for each soil type. All coefficients of the Langmuir linearized and non-linearized equations are shown in the supplementary data.

Data have fitted well to the Langmuir model for all studied REY and for the entire range of concentration for soils A, B, and E, which have all shown a high coefficient of determination (R^2) for both Langmuir equations (linearized and non-linearized) (supplementary data). As can be seen for these three soils, the adsorption of REY reached a plateau upon increasing the REY concentration added in the solution, which suggested a L-type isotherm. Such isotherm type indicates that the adsorption sites were being occupied with the increase in the REY concentration added (Sposito, 1989). It is well known that the isotherm shape, especially the slope, is commonly used to describe the behavior of the surface sites (Giles, 1974; Hinz, 2001). The initial slope in the isotherms suggested high affinity of these soils for REY retention. Certainly, the shape of soil A, B, and E curves are related to the organic carbon content and the mineral phases of each soil (described earlier) and, also, the type of complex (inner- or outher-sphere) that predominates in the sorption process. Several authors have mentioned that REY are sorbed mainly by inner-sphere complexes in different mineral phases (Laveuf and Cornu, 2009), such as 2:1 clays (Coppin et al., 2002) and oxides (Piasecki and Sverjensky, 2008b). Based on the fit of the Langmuir models and the calculated percentiles we have seen that REY_{MAC} in soil E was significantly higher than in all others soils, for all REY, while REY_{MBC} was significantly higher for soil A, for the REY's La, Ce, Pr, Nd, Gd, Dy, and Y.
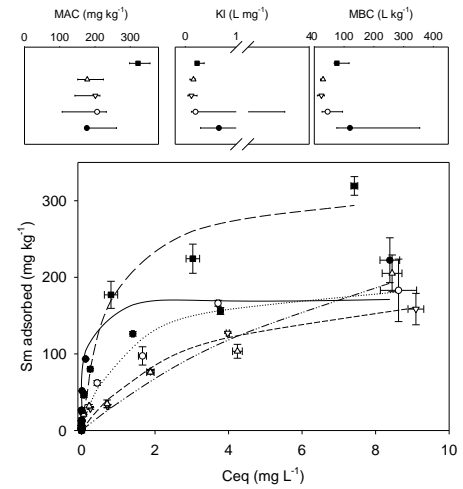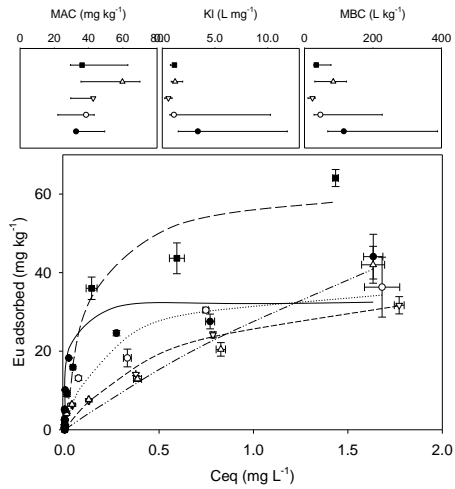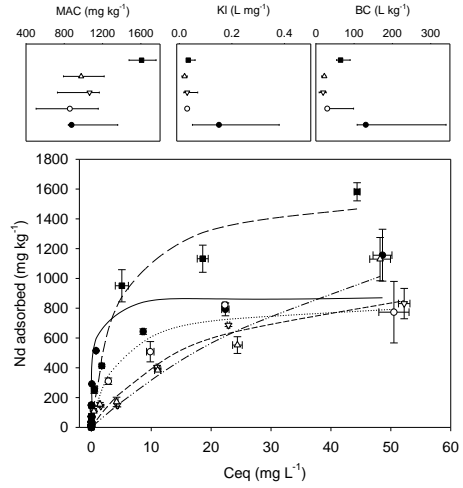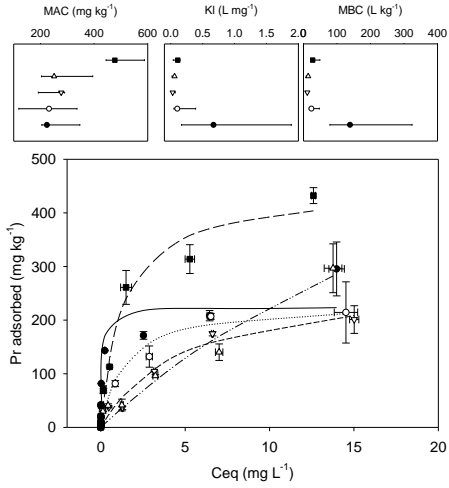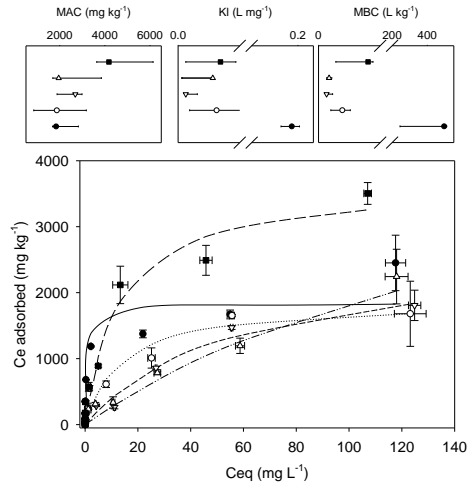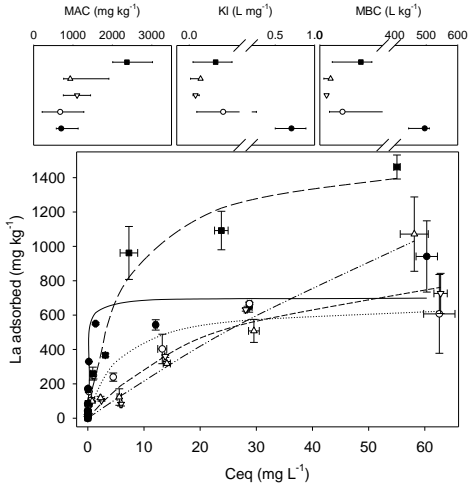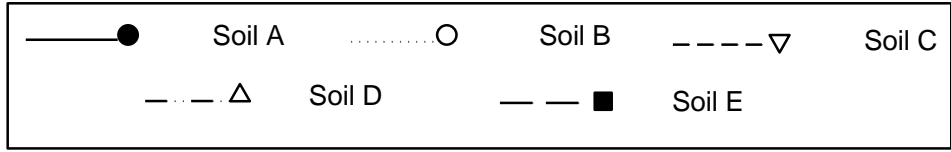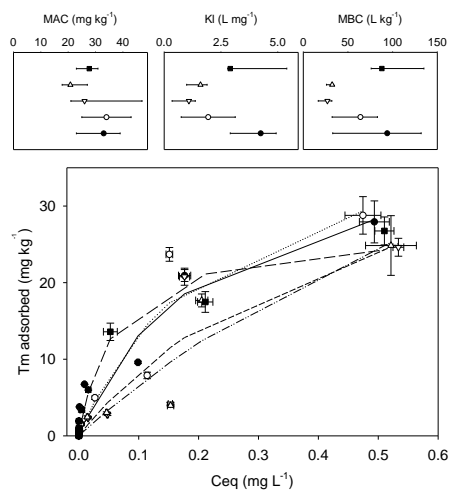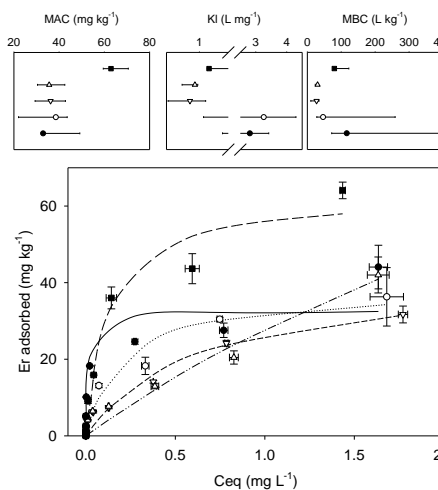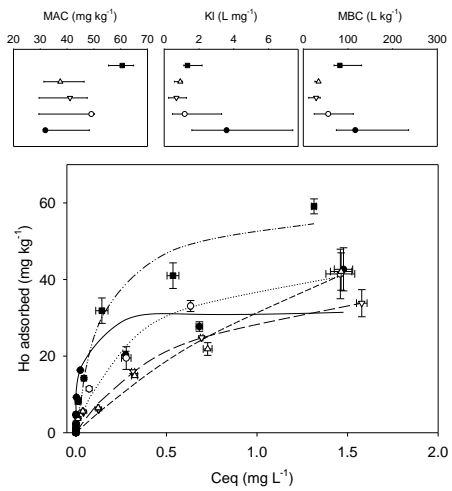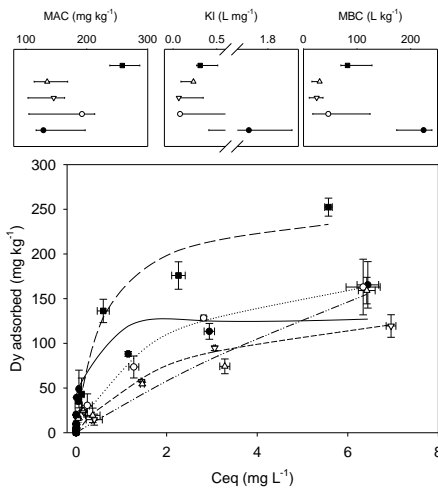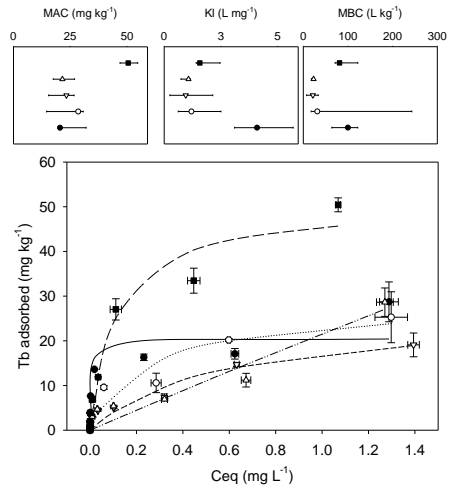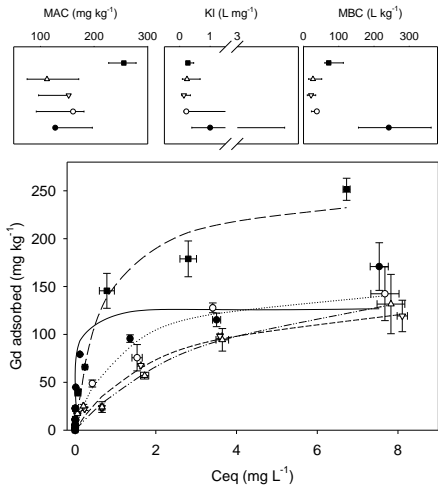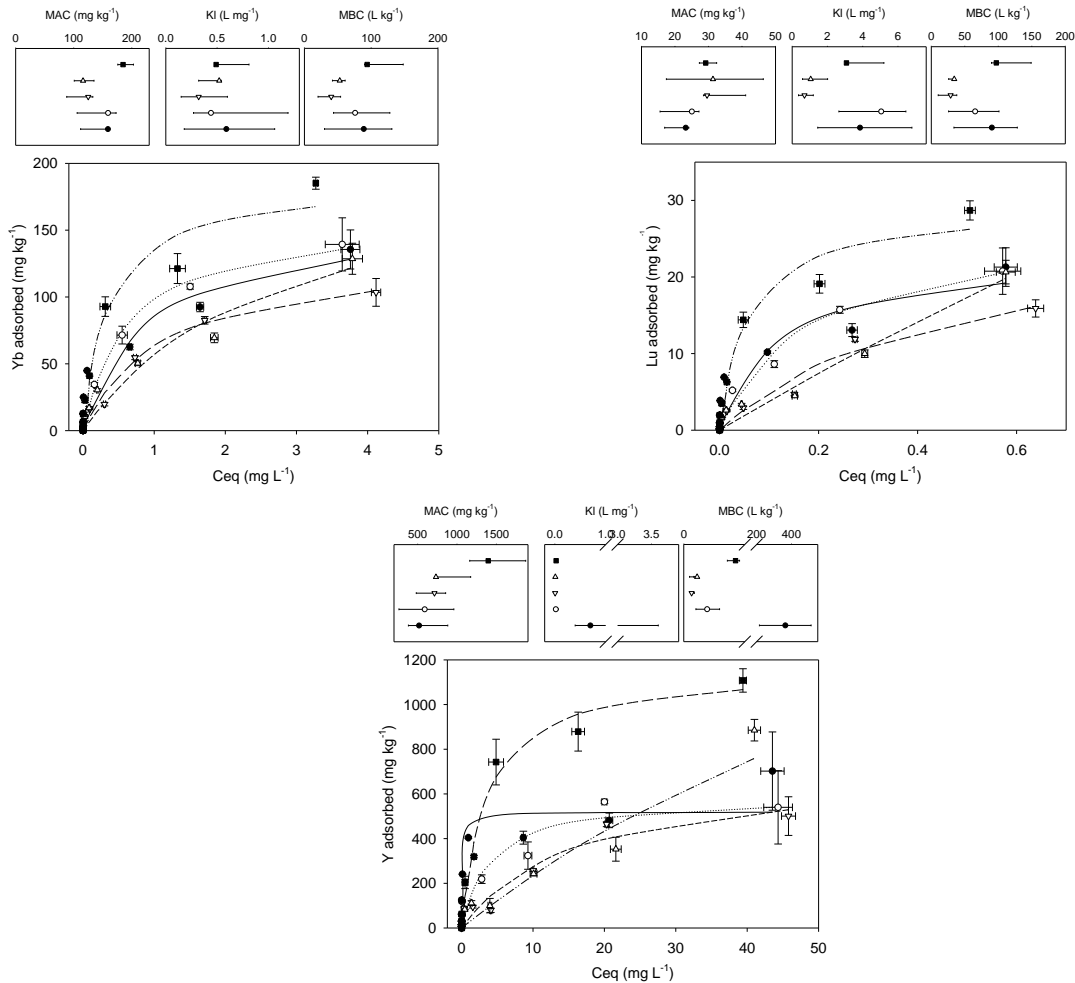
Figure 4: REY adsorption behavior by Langmuir model for all soils. Each point on the figures represents the mean from three replicate plots. The values over each graphic (three small graphic above) represent the 5th and 95th percentile of bootstrap replications of the REY_{MAC}, KL, and REY_{MBC} data set for each soil type.

Soils C and D, which are soils with high sand percentages (75 and 71%, respectively), showed high REY_{MAC}, similar to values observed for soil B (table 3). However, these soils did not fit very well to the Langmuir linear model, presenting low coefficients of determination. Such weak fits have attracted attention to the adsorption data. Actually, it is possible to realize two regions (or trends) in the adsorption isotherm for these soils, as it can be seen in the case of Ce in Figure 5. Note that the REY_{MAC} values showed in table 3 for soils C and D were overestimated by the Langmuir model, when compared with the first adsorption trend showed in Figure 5. For example, if taking into account data from the first "adsorption trend", the Langmuir model has revealed the following values for REY_{MAC}, KL, and REY_{MBC} for cerium in soils C and D: 260.61 mg kg^{-1}, 0.113 L mg^{-1}, and 59.94 L kg^{-1}, and

272.77 mg kg^{-1}, 0.192 L mg^{-1}, and 52.37 L kg^{-1}, respectively. Such values, especially for REY$_{MAC}$, are more appropriate for sandiers soils, as soils C and D.

Thus, REY$_{MBC}$ has shown to be a more accurate parameter to represent REY behavior for soils C and D. This is easily seen when soils C and D are compared with soil B. Note that in this comparison, the values of REY$_{MAC}$ are similar for all soils, while REY$_{MBC}$ is totally different, being higher for soil B, which differentiate this soil from the others. Therefore, since this study did not record data until reaching the maximum adsorption in the second "adsorption trend" of the REY, all data showed in table 3 for soils C and D must be used only as a reference for further studies. Consequently, more studies on REY adsorption, especially in sandier tropical soils, are needed in order to better understand the adsorption phenomena of such elements in the environment.
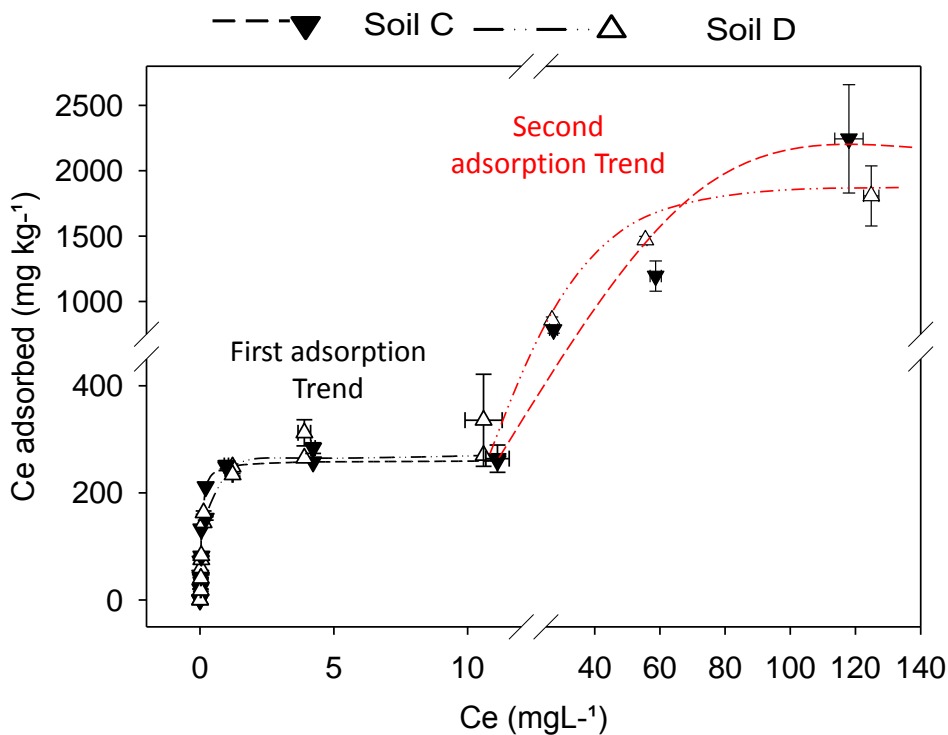
Figure 5: Adsorption trends observed for cerium for soils C and D.

REY Adsorption Signature

The REY$_{MAC}$ signatures are shown in Figure 6. These signature data were obtained from data of REY$_{MAC}$ divided by La-REY$_{MAC}$, which were then compared with the signature for UCC normalized values. It is well known that the REY have a peculiar behavior on the terrestrial crust, due to the geochemical and biochemical features inherent to them. They are the principal elements that respect the "Oddo-Harkins" rule. Also, it is widely accepted that this tool helps adjust the data for a better understanding of different environmental process. In the last decades, REY have been used as useful tracers in geochemical studies, due to their unique chemical structures (Wang et al., 2011).

However, to the best of our knowledge, until now no data was reported showing REY signatures for REY-sorption.

Our data on REY_{MAC} signatures have demonstrated the same behavior for the five studied soils and were similar to the signature verified for the upper continental crust. These data show the importance of REY as tracers in the environment. Moreover, the signatures found in this study are very similar to the data reported by Ramos et al. (2016b). These authors have observed a great similarity between the UCC signature and the REY signatures for total REY levels in soils worldwide, even after anthropogenic actions. The REY_{MAC} signatures together with data from literature suggest that irrespectively of the REY concentration, REY behavior in soils (signatures) has the tendency to find a balance according to the intrinsic characteristics in each element. This fact was also shown for raw materials and phosphate fertilizers elsewhere (Ramos et al., 2016a).
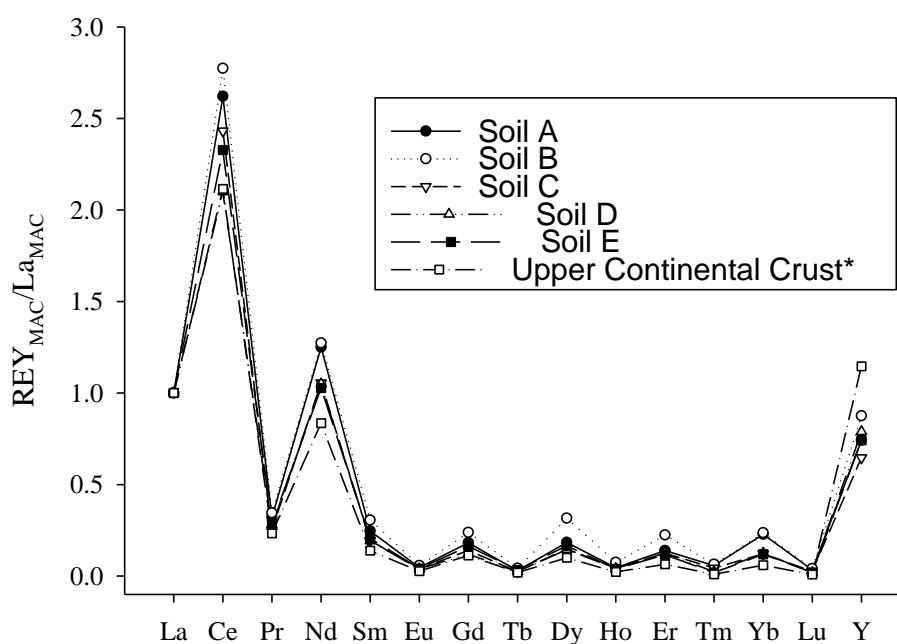
Figure 6: REY adsorption signatures for all studied soils. * Data from Taylor and Mclennan (1995).

4–Conclusion

This study has provided information about REY adsorption on soils. It has shown that besides the clay content, clay type and organic matter content are also important for soil REY buffering capacity. Considering REY's "natural" molar concentration, cerium sorption was the highest - and lutetium's the lowest -, independently of the soil characteristics. The Langmuir model was not

adequate to fitting adsorption data for sandy tropical soils. REY_{MBC} has shown to be a good parameter for comparing REY behavior at the soil-solution interface.

The REY sorption signatures have followed the same signature for the UCC levels. Also, it seems that REY sorption trends follow the same signature as they are introduced on soil, REY concentration signature = REY sorption signature. Finally, our findings may be beneficial and useful toward a better understanding of REY behavior in agroecosystems. However, further studies with the inclusion of many soils with broader physical-chemical characteristics are still needed to reinforce the usefulness of the parameters here discussed

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6 – References

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Supplementary data

Table A - KL, REY$_{MAC}$ parameter of the Langmuir isotherms from linearized and non-linearized model as well as the REY$_{MBC}$ for all five soils.

	Soil A								Soil B								R²
	Linear parameters				Non linear parameters*				Linear parameters				Non linear parameters*				
	KL	REY MAC	REY MBC	R²	KL	REY MAC	REY MBC	R²	KL	REY MAC	REY MBC	R²	KL	REY MAC	REY MBC		
	l mg^{-1}	mg kg^{-1}	l kg^{-1}		l mg^{-1}	mg kg^{-1}	l kg^{-1}		l mg^{-1}	mg kg^{-1}	l kg^{-1}		l mg^{-1}	mg kg^{-1}	l kg^{-1}		
La	0.141	5693.3	799.9	0.98	0.706	701.1	495.3	0.94	0.120	2847.6	341.7	0.96	0.027	674.17	18.1		0.91
Ce	0.060	15335.2	918.1	0.97	0.196	1837.4	360.8	0.90	0.051	9493.6	479.8	0.97	0.010	1869.77	19.3		0.95
Pr	0.558	1856.6	1035.3	0.98	1.893	224.5	424.9	0.91	0.648	1262.2	818.1	0.98	0.102	232.34	23.8		0.95
Nd	0.142	7162.4	1015.5	0.97	0.389	876.7	340.9	0.90	0.142	5212.3	741.5	0.98	0.035	858.48	29.9		0.95
Sm	0.877	1352.9	1186.9	0.97	2.054	172.6	354.5	0.91	0.782	1047.4	819.5	0.98	0.127	206.05	26.1		0.96
Eu	3.974	256.7	1020.2	0.95	11.859	32.7	388.2	0.89	3.669	206.4	757.3	0.98	0.725	38.57	28.0		0.95
Gd	0.976	970.6	947.6	0.97	3.629	127.5	462.9	0.90	0.707	812.8	574.3	0.97	0.141	160.82	22.6		0.95
Tb	5.368	155.1	832.8	0.94	31.557	20.5	646.6	0.98	3.503	132.6	464.6	0.93	0.621	28.56	17.7		0.91
Dy	1.137	902.6	1026.6	0.97	1.738	129.0	224.2	0.99	0.636	883.5	562.1	0.95	0.082	213.03	17.5		0.97
Ho	3.916	230.6	903.2	0.95	7.392	31.9	235.9	0.97	2.815	230.6	649.0	0.96	0.489	50.23	24.6		0.97
Er	1.365	689.0	940.6	0.95	2.168	97.5	211.5	0.98	0.656	718.3	471.0	0.90	0.199	150.86	30.1		0.98
Tm	7.529	155.3	1169.0	0.89	0.832	39.9	33.2	0.95	3.853	161.8	623.2	0.73	0.744	43.42	32.3		0.91
Yb	1.540	721.6	1111.3	0.95	0.189	159.6	30.1	0.93	1.263	753.6	952.0	0.97	0.274	159.26	43.7		0.99
Lu	9.653	108.6	1048.5	0.94	1.456	23.2	33.8	0.91	6.299	109.5	689.8	0.94	0.953	27.17	25.9		0.98
Y	0.148	6326.3	799.9	0.99	0.701	520.0	364.6	0.91	0.210	4697.9	986.2	0.97	0.023	590.02	13.4		0.92

* Parameters of Langmuir isotherms estimated by the "sums of square" methods using Microsoft Excel Solver[®].

Table A – continuity…

	Soil C								Soil D							
	Linear parameters				Non linear parameters*				Linear parameters				Non linear parameters*			
	KL	REY MAC	REY MBC	R²	KL	REY MAC	REY MBC	R²	KL	REY MAC	REY MBC	R²	KL	REY MAC	REY MBC	R²
	$l\,mg^{-1}$	$mg\,kg^{-1}$	$l\,kg^{-1}$		$l\,mg^{-1}$	$mg\,kg^{-1}$	$l\,kg^{-1}$		$l\,mg^{-1}$	$mg\,kg^{-1}$	$l\,kg^{-1}$		$l\,mg^{-1}$	$mg\,kg^{-1}$	$l\,kg^{-1}$	
La	0.016	5378.0	84.0	0.63	0.005	1105.2	5.4	0.91	0.009	6698.8	61.8	0.54	0.009	930.5	8.6	0.95
Ce	0.010	13016.7	132.4	0.78	0.002	2687.9	6.5	0.97	0.009	13938.1	119.0	0.72	0.009	1953.0	16.7	0.98
Pr	0.113	1431.4	162.3	0.87	0.028	277.2	7.9	0.97	0.069	1781.2	122.8	0.66	0.069	251.0	17.3	0.97
Nd	0.032	5755.7	181.9	0.86	0.007	1166.7	8.7	0.98	0.023	6768.1	153.7	0.73	0.023	976.2	22.2	0.97
Sm	0.222	1035.7	229.8	0.90	0.049	214.5	10.5	0.98	0.164	1189.1	195.5	0.78	0.164	178.8	29.4	0.97
Eu	1.200	205.2	246.3	0.91	0.240	42.8	10.3	0.98	0.850	234.3	199.0	0.76	0.850	35.6	30.2	0.97
Gd	0.268	747.1	199.9	0.90	0.070	154.6	10.8	0.98	0.240	713.0	171.4	0.87	0.240	112.1	27.0	0.98
Tb	1.658	113.2	187.7	0.89	0.278	26.7	7.4	0.96	1.073	135.6	145.4	0.65	1.073	21.5	23.1	0.95
Dy	0.285	732.9	208.7	0.87	0.066	163.6	10.8	0.98	0.233	830.5	193.9	0.76	0.233	134.9	31.5	0.97
Ho	1.171	202.6	237.2	0.87	0.258	47.5	12.3	0.99	0.927	227.1	210.6	0.78	0.927	37.5	34.7	0.98
Er	0.217	641.1	139.2	0.49	0.100	137.7	13.8	0.99	0.308	702.2	216.5	0.76	0.308	117.5	36.2	0.97
Tm	1.494	134.1	200.4	0.36	0.353	47.6	16.8	0.94	1.606	123.2	197.9	0.39	1.606	20.8	33.4	0.91
Yb	0.558	599.5	334.6	0.71	0.153	133.6	20.4	0.99	0.528	670.4	353.9	0.87	0.528	116.0	61.2	0.96
Lu	2.448	88.3	84.0	0.76	0.367	28.3	10.4	0.96	2.015	99.7	200.9	0.62	2.015	17.4	35.1	0.98
Y	0.021	5604.6	132.4	0.81	0.006	714.8	4.0	0.95	0.010	8251.5	61.8	0.45	0.010	733.6	7.6	0.95

* Parameters of Langmuir isotherms estimated by the "sums of square" methods using Microsoft Excel Solver®.

Table A – continuity…

Soil E							
Linear parameters				Non linear parameters*			
KL	REY$_{MAC}$	REY$_{MBC}$	R²	KL	REY$_{MAC}$	REY$_{MBC}$	
l mg^{-1}	mg kg^{-1}	l kg^{-1}		l mg^{-1}	mg kg^{-1}	l kg^{-1}	R²
0.06	10323.3	574.24	0.96	0.021	1564.3	32.7	0.99
0.03	24279.5	755.63	0.96	0.011	3641.5	40.2	0.97
0.30	2993.4	887.40	0.97	0.110	444.9	49.0	0.98
0.09	10663.9	945.45	0.97	0.034	1607.7	54.4	0.98
0.57	2059.3	1170.72	0.97	0.208	322.4	67.1	0.98
3.03	406.2	1228.86	0.96	1.233	63.0	77.6	0.97
0.64	1546.4	984.32	0.96	0.238	255.3	60.7	0.98
3.77	305.1	1150.58	0.95	1.410	50.5	71.2	0.97
0.78	1506.9	1181.33	0.96	0.270	258.3	69.8	0.98
3.19	348.2	1112.24	0.96	1.137	60.6	68.9	0.98
0.89	1045.6	931.89	0.94	0.416	182.7	76.0	0.97
8.04	151.0	1214.03	0.95	2.801	27.1	76.1	0.97
1.31	1030.8	1355.44	0.95	0.486	185.9	90.4	0.97
8.47	158.9	1345.65	0.96	3.080	29.2	89.9	0.97
0.07	12279.0	838.82	0.98	0.026	1161.0	29.7	0.98

* Parameters of Langmuir isotherms estimated by the "sums of square" methods using Microsoft Excel Solver®.