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ARTICLE



Lixiviation of rare earth elements in tropical soils amended with phosphogypsum

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ABSTRACT

In Brazil, the main producers of phosphate fertilisers are responsible for the production of approximately 12 million tons of phosphogypsum (PG) per year. This phosphogypsum has been used for many years in agriculture as a soil amendment. For its safe long-term application, it is necessary to characterise the impurities present in phosphogypsum and to study the leaching or dissemination of such impurities to waters or other ecosystem compartments. This paper aims to evaluate the availability of Rare Earth Elements (REEs): La, Ce, Nd, Sm, Eu, Tb and Lu. The technique used for the determination of the elements of interest in the soil, soil mixed with PG, PG and leachate was the instrumental neutron activation analysis. For this purpose, an experiment was carried out, in which columns filled with sandy and clay Brazilian typical soils mixed with phosphogypsum were percolated with water, to achieve a mild extraction of these elements. The results showed that the Σ REE in PG was in the order of $7,600 \text{ mg kg}^{-1}$ while in the leachate, the sum was in the order of $100 \mu\text{g L}^{-1}$ results obtained for the available fraction obtained was below 1%, giving evidence that although the REEs are present in the PG in higher concentrations, they are not available to the water. It can be concluded that the addition of PG to the soils does not contribute to a significant enhancement of the REEs in water.

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1. Introduction

The presence of impurities, such as radionuclides, metals and rare earth elements (REEs) in mineral ores and their redistribution in industrial products and wastes is well known [1–3]. Brazilian fertiliser industries produce phosphoric acid by reacting phosphate rocks with sulphuric acid giving as by-product phosphogypsum (PG) [4]. Phosphoric acid is the starting material for the most utilised Brazilian fertilisers: triple superphosphate, single superphosphate, mono ammonium phosphate and diammonium phosphate [5]. The main constituent of the Brazilian phosphate rock is the apatite (carbonatite) of igneous origin [6]. The REEs are present in this mineral as minor elements, although mass fraction

higher than $1,000 \mu\text{g g}^{-1}$ had been reported [7], with a variation of 20% in their concentration [8].

In Brazil, the extraction of the phosphate rock occurs mainly in the cities of Tapira, Araxá, Catalão, and Cajati (in the States of Minas Gerais, Goiás and São Paulo), with phosphorus pentoxide (P_2O_5) content of 10% [9]. The rock concentrate, up to 37% of P_2O_5 , is then transported to other locations, where it will be processed to phosphoric acid. The main Brazilian producers of phosphoric acid and phosphogypsum are located in Uberaba and Cubatão [9].

The main producers of phosphate fertilisers, in Brazil, are responsible for the production of approximately 12 million tons of phosphogypsum per year. This phosphogypsum has been used for many years in agriculture as a soil amendment [10]. For its safe long-term application, it is necessary to characterise the impurities present in phosphogypsum and to study the leaching or dissemination of such impurities to waters or other ecosystem compartments and consequent impact in the food chain [11–13].

The main reserves of REE are found in carbonatite rocks located in Angico dos Dias complex in the State of Bahia ($7,483 \mu\text{g g}^{-1}$), Araxá in Minas Gerais State ($6,347 \mu\text{g g}^{-1}$), and Catalão in Goiás State ($5,585 \mu\text{g g}^{-1}$) [14]. The distribution of REE in apatite depends mainly on the rock origin. The igneous apatite presents a progressive change in its composition, from pegmatitic granites, more rich in heavy lanthanides and yttrium, to alkaline pegmatites and carbonatites, richer in light lanthanides [15].

Besides the increasing use of REE in high-tech industries, one of the main sources of these elements in soils is due to the use of fertiliser phosphates and PG enriched in these elements in agriculture [16,17]. Although some studies have shown that REE may improve plant growth [18,19], they are not essential for human health and their behaviour, when ingested, is poorly understood. Despite this, it is known that they can accumulate in blood, lungs, liver, brain, and bone tissue [20–22]. Considering that there is also little information about REE mobility in the environment and that phosphogypsum has been used for many years in Brazil as soil amendment, it is important to characterise these elements in the Brazilian phosphogypsum and to evaluate their leaching. In recent literature, few data are available related to the presence of rare earth elements and their distribution in the phosphate industry in Brazil [10,23].

Effects of REE in the biota have been documented by MacMillan et al. [24], Amyot et al. [25], Agathokleous [26] and Herrmann et al. [27]. In general, REEs accumulate in lichen and moss, marine and freshwater invertebrates, fish, benthic macroinvertebrates, and zooplankton. Low concentrations of REE can stimulate plants growth, high concentration, on the other hand, can inhibit the growth of both terrestrial and marine plants. It is also important to consider that although applications in agriculture still remain the main source of REE in the environment, the increase of high-technology applications in medicine, mobile communication, energy, and electronics can enhance the anthropogenic input of these elements, resulting in contamination of the environment [28]. The short-term and long-term environmental impact of REE released to soils will depend on their solubility, ionic exchange capacity and formation of chelates, since these chemical species correspond to the labile fractions that will be available to the food chain [29]. Šmuc et al. [30] studied the TF of REE from paddy soil to rice system. The TF values observed by them ($\sim 4.5 \times 10^{-4}$) are of the same order of magnitude of those obtained by Nakamaru et al. [31] for soybean stems and seeds.

Mazzilli et al. [10] carried out an experiment on a greenhouse, where soya bean, corn and lettuce were grown in two types of soil (clay and sandy) amended with Brazilian phosphogypsum. They evaluated the transfer-factor for metals, REEs and natural radionuclides. The addition of PG to the two soils studied did not significantly alter the transfer-factor values for all the elements studied.

Mazzilli & Saueia [23] evaluated the availability of radionuclides and REEs (La, Ce, Nd, Sm, Eu, Tb, and Lu) present in phosphogypsum, by leaching with water and ethylenediaminetetraacetic acid (EDTA) solution. The results of the extraction with water showed that, although the high dissolution of PG (~90%), less than 1% of the REEs were extracted; whereas, for the extraction with EDTA solution only 10% of the PG mass was dissolved and small amounts of Ce and La were extracted.

More recently, an experiment was conducted in the laboratory, in which columns filled with Brazilian typical sandy and clay soils and phosphogypsum were percolated with water, in order to achieve a mild extraction of radionuclides and metals [32]. The availability of radionuclides and metals was evaluated by measuring the total concentration in the mixture of soil and phosphogypsum and the concentration in the leachate. As a complementary study, this paper aims to evaluate the availability of REEs (La, Ce, Nd, Sm, Eu, Tb and Lu). The technique used for the determination of the elements of interest in the soil, soil mixed with PG, PG and leachate was the instrumental neutron activation analysis.

2. Experimental

2.1. Soil sampling and soil preparation

The leachate tests performed in this study used two different types of soil, sandy and clayey, collected in the countryside of São Paulo State, in Piracicaba region. The chemical analysis of the soils showed that they are considered dystrophic, with base saturation (V%) lower than 50, justifying the necessity of the soil correction with phosphogypsum [32]. Brazilian phosphogypsum from two provenances was used in the experiment, one from Uberaba (PG UBE) and the second from Cubatão (PG CUB). The soils samples, as well as the PG samples used in this study, are described for their chemical characteristics in Nisti et al. [32]. Both, soil and PG, were treated following the methodology described in the same paper. PVC columns (60 cm long × 14 cm diameter) were filled with the clay and sandy soils, the PG from two provenances, mixtures of soil plus the recommended dose of PG (D1) and mixtures of soil plus 10 times the recommended PG dose (D10) to simulate long-term applications, totalising 12 columns. Every set of experiment was performed in triplicate. The total volume of samples inside the column was 0.00385 m³. All the columns were saturated initially with distilled water in order to achieve their field capacity. The field capacity was determined experimentally for each type of column: 1,400 mL for sandy soil; 2,100 mL for clay soil and 1,000 mL for PG samples, to ensure that the samples were completely saturated. After 48 h, the same volume of 2,300 mL of the leaching water was percolated through the columns. The volume of water added considered 1/12 of the annual average rainfall of the State of São Paulo. After the percolation, all the leachate was collected and used for the determination of the REE concentration. During the tests, any significative differences were not observed in the percolation rate among the different samples. The

Table 1. Relative standard deviation (RED) and relative error (ER), given in per cent (%), obtained for the measurement of La, Ce, Nd, Sm, Eu, Tb and Lu in the reference materials IAEA – SL3 Lake Sediment and NIST-Montana II Soil.

	La	Ce	Nd	Sm	Eu	Tb	Lu
RSD	2.1	7.5	7.2	1.4	1.5	7.1	3.3
RE	4.4	3.9	3.8	6.3	5.9	4.6	4.5

concentrations of the REE extracted by this procedure represent, therefore, the amount that is available by the addition of water to a saturated soil.

2.2. Determination of REE in soil, soil mixed with PG, PG and leachate samples by instrumental neutron activation analysis

The REEs were determined by instrumental neutron activation analysis (INAA) [33,34]. The determination was carried out by irradiation of approximately 150 mg of each solid sample, 100 mL of leachate sample and 150 mg of reference materials, in the research reactor IEA-R1, during 8 h at a neutron flux of 10^{12} n.cm⁻²s⁻¹, at Instituto de Pesquisas Energéticas e Nucleares (IPEN).

The solid samples were packed in polyethylene bags, sealed and irradiated with reference material under the same conditions. For the leached solution, 100 mL of the sample was heated to volume reduction and pipetted into a paper filter, dried in an infrared lamp, then conditioned and irradiated under the same conditions as the standard solutions.

After irradiation, the samples measurement was undertaken by gamma spectrometry, using a detector from INTERTECHNIQUE with relative efficiency of 25% and resolution of 2.1 keV for the 1,332 keV peak of ⁶⁰Co. The first count was made after 5 to 10 days of decay and allows identifying La, Nd, Sm and Tb. The second count was made after 15 days of decay and allows identifying Ce, Eu and Lu. The accuracy and precision were performed by measuring the Standard Reference Materials IAEA-SL3-Lake Sediment and NIST-Montana II Soil. In Table 1, the precision and accuracy obtained by the calculation of relative standard deviation (RSD) and relative error (RE), respectively, for the measurement of La, Ce, Nd, Sm, Eu, Tb and Lu in the reference materials IAEA- SL3 Lake Sediment and NIST-Montana II Soil are presented.

3. Results and discussion

The elements La, Ce, Nd, Sm, Eu, Tb and Lu were analyzed in triplicate in samples of soil, soil + PG and PG by INAA technique. The average concentration of the elements Ce, Eu, La, Lu, Nd, Sm and Tb is presented in Table 2, together with the concentration in the Continental Crust [35]. The REEs concentration in the clay soil is slightly above the reference level of the continental crust, whereas the sandy soil present values below the reference levels. The REE concentration in the clay soil is higher than the sandy soil; the results are in good agreement with literature values for Brazilian soils [36,37]. The phosphate rock concentrate used in Cubatão installation comes from Catalão mine and presents REE concentration showed in Table 2. The values show that REEs are mostly transferred to PG during the fertiliser production process. For comparison Table 2 also

Table 2. Average concentration of La, Ce, Nd, Sm, Eu, Tb and Lu in samples of soil, soil + PG and PG and reference values of the Continental Crust (mg kg⁻¹).

Sample description	La	Ce	Nd	Sm	Eu	Tb	Lu
PG CUB	1,750 ± 79	3,400 ± 160	2,180 ± 70	167 ± 3	40 ± 2	13 ± 1	0.2 ± 0.1
PG UBE	820 ± 29	1,540 ± 37	1,000 ± 52	98.0 ± 3.8	21 ± 4	9.9 ± 0.3	0.38 ± 0.05
Sandy soil	3.2 ± 0.3	6.1 ± 0.9	3.27 ± 1.84	0.37 ± 0.07	0.09 ± 0.01	0.2 ± 0.1	0.11 ± 0.04
Sandy soil + PG CUB_D1	7 ± 3	14 ± 5	9 ± 4	0.7 ± 0.2	0.14 ± 0.03	0.2 ± 0.1	0.10 ± 0.01
Sandy soil + PG CUB_D10	27 ± 3	56 ± 7	37 ± 8	3.0 ± 0.5	0.6 ± 0.1	0.22 ± 0.04	0.11 ± 0.01
Sandy soil + PG UBE_D1	4.7 ± 0.6	9 ± 2	10 ± 2	0.57 ± 0.08	0.11 ± 0.01	0.27 ± 0.04	0.09 ± 0.02
Sandy soil + PG UBE_D10	14 ± 4	26 ± 7	10 ± 1	1.5 ± 0.3	0.4 ± 0.1	0.49 ± 0.04	0.10 ± 0.01
Clay soil	33.8 ± 0.6	116 ± 2	22 ± 2	5.5 ± 0.3	1.26 ± 0.06	0.89 ± 0.05	0.37 ± 0.03
Clay soil + PG CUB_D1	35 ± 2	116 ± 6	49 ± 10	5.3 ± 0.2	1.1 ± 0.2	0.8 ± 0.7	0.34 ± 0.03
Clay soil + PG CUB_D10	43 ± 3	139 ± 3	25 ± 12	6.3 ± 0.4	1.9 ± 0.1	2.3 ± 0.5	0.38 ± 0.03
Clay soil + PG UBE_D1	34.3 ± 0.3	107 ± 12	27 ± 3	5.4 ± 0.1	1.28 ± 0.05	1.5 ± 0.1	0.40 ± 0.02
Clay soil + PG UBE_D10	37.3 ± 0.8	119 ± 7	27 ± 6	5.8 ± 0.1	1.31 ± 0.03	0.8 ± 0.2	0.42 ± 0.02
Detection limit	<1	<2.5	<2.1	<0.04	<0.2	<0.3	< 0.05
Catalão Phosphate rock concentrate ^d	2,220 ± 530	5,310 ± 1,160	1,490 ± 410	256 ± 24	68 ± 8	13.0 ± 4.9	0.65 ± 0.13
Belgian phosphogypsum ^c	1,450	2,310	899	163	34.9	7.45	0.568
Tunisian phosphogypsum ^b	54.42	96.73	59.42	9.63	2.29	1.46	0.65
Continental Crust ^a	30	60	27	5.3	1.3	0.65	0.35

D1 = Recommended PG dose; D10 = 10 × the recommended PG dose.

^aWedepohl [27,35].^bHammam-Nasri et al. [30,36].^cBinnemans et al. [31,37].^dOliveira et al. [29,37].

presents the REE concentration in Tunisian and Belgian PG [38,39]. The differences observed depend on the phosphate rock used as raw material. For the two analyzed installations, the values are in good agreement with literature values [7].

The distribution of the REE in the two types of soil and in the mixture of soil with PG is depicted in Figure 1 and values found in the clay soil analyzed in this study were like that reported by [30,31]. The effect of the PG addition in clay and sand soil is shown in Figure 2. The t-test for independent samples was applied, lowercase letters were used to compare the addition of PG in clay soil and uppercase letters for sand soil. The addition of PG to the clay soil did not increase significantly the final concentration in the mixture except for the light rare earth elements, when PG from Cubatão was applied in the concentration 10 times higher the recommended dose, for La in the application of the Uberaba PG in the same concentration (D10), and for Tb in the recommended dose (D1). A significant higher amount of Nd was also observed after the application of PG from Cubatão, in the recommended dose, in clay soil, but this fact can be related to the higher uncertainties associated to the determination of this element. For sand soil, the application of 10 times the recommended dose of PG significantly increased the amount of all REEs, except Lu.

The elements La, Ce, Nd, Sm, Eu, Tb and Lu were analyzed in the leachate solution by INAA technique. The average concentrations of the elements in the leachate are presented in Table 3. The results obtained show that the concentrations found in the leachate are lower than the concentration present in the soil, soil + PG and PG with

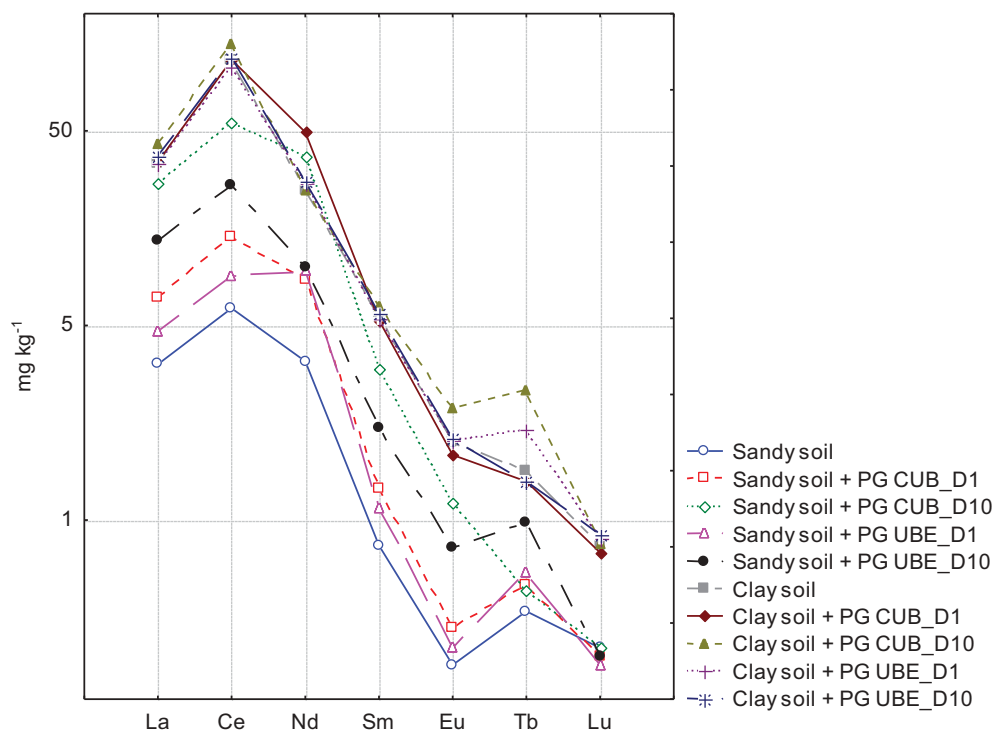


Figure 1. Average concentration (mg kg^{-1}) of La, Ce, Nd, Sm, Eu, Tb and Lu in samples of soil, soil + PG.

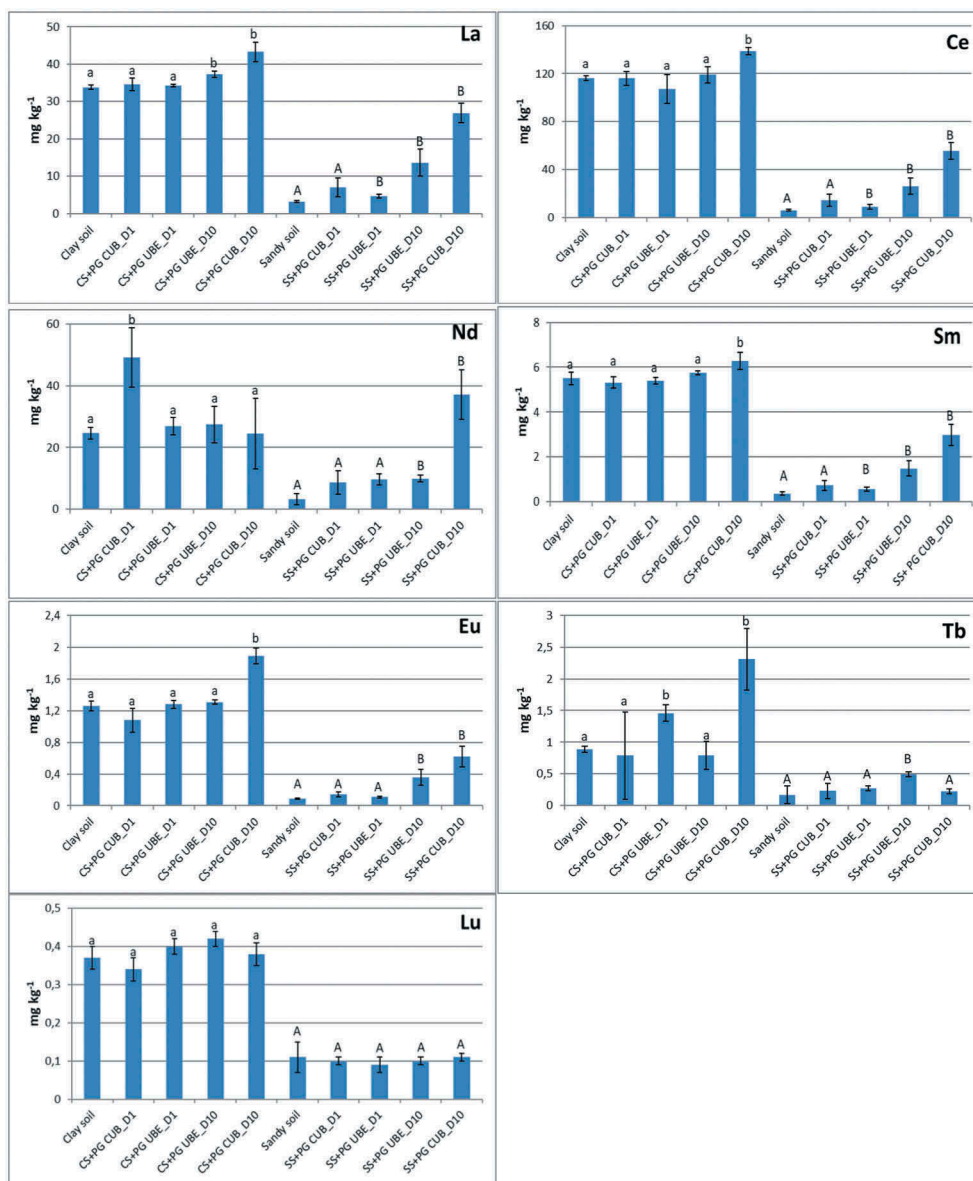


Figure 2. Average concentration (mg kg^{-1}) of La, Ce, Nd, Sm, Eu, Tb and Lu in samples of soil, soil + PG. Lowercase refers to clay soil and clay soil + PG, uppercase refers to sand soil and sand soil + PG. Same letters means no statistical difference, different letters means statistical differences between the average concentrations.

a partition coefficient around 10^3 . Values higher than the detection limits were found for almost all light REEs in the leachate of the mixture sand soil + PG both in the recommended dose and in the dose 10 times higher, indicating that, although in very small amounts, the long-term application of PG enriched in REE may transfer these elements to the environment. All the values found in the leachate are also higher than those found for soil only, indicating that most of the REE leachate comes from the PG. In



Table 3. Average concentration of La, Ce, Nd, Sm, Eu, Tb and Lu in the leachate of soil, soil + PG and PG ($\mu\text{g L}^{-1}$).

Sample description	La	Ce	Nd	Sm	Eu	Tb	Lu
PG CUB	57 ± 2	53 ± 3	26 ± 5	3 ± 2	1.64 ± 0.06	0.4 ± 0.1	<0.07
PG UBE	238 ± 7	102 ± 27	112 ± 59	19 ± 8	5 ± 1	3 ± 2	0.37 ± 0.05
Sandy soil	1.1 ± 0.2	2.84 ± 0.02	<23.9	<0.6	0.04 ± 0.01	<0.3	<0.07
Sandy soil + PG CUB_D1	27 ± 13	46 ± 21	<23.9	1.43 ± 0.06	0.5 ± 0.1	<0.3	<0.07
Sandy soil + PG CUB_D10	60 ± 16	83 ± 21	24 ± 2	4.2 ± 0.5	1.03 ± 0.08	<0.3	<0.07
Sandy soil + PG UBE_D1	15 ± 3	30 ± 7	<23.9	<0.6	0.5 ± 0.4	<0.3	<0.07
Sandy soil + PG UBE_D10	45 ± 17	60 ± 23	<23.9	2 ± 1	0.7 ± 0.3	<0.3	0.09 ± 0.02
Clay soil	< 1	< 2.2	<23.9	<0.6	< 0.10	<0.3	<0.07
Clay soil + PG CUB_D1	< 1	< 2.2	<23.9	<0.6	< 0.10	<0.3	<0.07
Clay soil + PG CUB_D10	12.4 ± 0.8	12.1 ± 0.09	<23.9	0.70 ± 0.08	0.19 ± 0.04	<0.3	<0.07
Clay soil + PG UBE_D1	< 1	< 2.2	<23.9	<0.6	< 0.1	<0.3	<0.07
Clay soil + PG UBE_D10	25 ± 11	25 ± 10	<23.9	0.8 ± 0.1	0.28 ± 0.05	<0.3	<0.07
Detection limit	<1	<2.2	<23.9	<0.6	<0.1	<0.3	<0.07

D1 = Recommended PG dose; D10 = 10 × the recommended PG dose.

the leachate of clay soil amended with PG, REEs were only found in the higher dose. Although the concentrations of REE in the Cubatão PG are higher than that of the Uberaba PG, the concentrations in the leachate in the former are lower, indicating that part of the rare earth should migrate to a more soluble fraction during the phosphogypsum production. This fact, however, does not seem to affect the mobility of these elements when PG is mixed with both types of soils.

The available fraction, obtained by the ratio of the REE concentration found in the leachate and the corresponding concentration found in the soil and PG samples, was in all cases below 1%, giving evidence that although the REEs are present in PG in higher concentrations, they are slightly available to the water. Similar trend was also observed by Mazzilli & Saueia [23], who studied the leachability of REE present in PG, in water and EDTA. According to them, the results of the leaching with water showed that, although the high dissolution of PG (~90%), less than 1% of the REEs were extracted. The solubility of REE in natural water is mainly dependent on the phosphate and carbonate precipitation, coprecipitation and complex formation [40]. REE-phosphates and REE-carbonates are highly insoluble under the environmental condition which can be the reason for the very low mobility observed in this study.

4. Conclusions

The results obtained for the activity concentrations of the REEs in the clay soil are approximately one order of magnitude higher than the sandy soil and can be considered as background levels for the region studied. The results obtained for the PG samples showed enrichment in REEs concentration, and consequently an increase in the final concentration of the mixture soil plus PG. However, the available fraction obtained was below 1%, giving evidence that although the REEs are present in the PG in higher concentrations, they are slightly available to the water. It can be concluded that the addition of PG to the soils, even in quantities that exceeded 10 times the amount of phosphogypsum necessary to achieve 50% of the soil base saturation, should not contribute significantly to an enhancement of the REE in the water system. The low mobility and low leachability of REE in PG, as well as the low TF from soil to plants reported in the literature indicate that the potential threat to human health is not significant. However, since there are gaps in the knowledge about the environmental behaviour and fate of REE released to the environment, the results obtained in this study contribute for a better understanding of the availability of these elements in the environment.

Disclosure statement

No potential conflict of interest was reported by the authors.

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