RESEARCH ARTICLE

Identification of potential plant species hyperaccumulating light rare earth elements (LREE) in a mining area in Minas Gerais, Brazil

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Abstract

Phytoextraction of rare earth elements (REE) from contaminated soils has gained importance during the last few decades. The Poços de Caldas municipality in Brazil is known for its mineral richness, including large reserves of REE. In this study, we report light REE (La, Ce, Sm, Pr, and Nd) in soils and plants collected in an area. Composite soil samples and plant individuals were collected, and total concentrations of LREE in soils were determined by wavelength dispersive X-ray fluorescence (WDXRF). The plant available LREE concentrations in soils were estimated upon the acetic acid method (F1 fractions) of the stepwise sequential extraction procedure, together with plant content that was analysed by inductively coupled plasma mass spectrometry (ICP-MS). The total sum concentrations of tested LREE in soils varied from 5.6 up to 37.9 g kg^{-1}, the bioavailable fraction was *ca.* 1%, and a linear relationship was found between them. The only exception was Sm, whose availability was lesser and did not show a linear relationship. The concentration of LREE in non-accumulator plants varied from 1.3–950 mg kg^{-1} for Ce, La 1.1–99 mg kg^{-1}, Sm 0.04–9.31 mg kg^{-1}, Pr 0.1–24.1 mg kg^{-1}, and Nd 0.55–81 mg kg^{-1}. The concentration of LREE among shoots did not show a linear relation either with the available fraction or total content. The screening also revealed *Christella dentata* (Forssk.) Brownsey & Jermy, *Thelypteridaceae* family, as a promising hyperaccumulator species. The concentrations of LREE among shoots of six individuals of this species were in the ranges from 115 to 1872 mg kg^{-1} for Ce, La 190–703 mg kg^{-1}, Sm 9–48 mg kg^{-1}, Pr 32–144 mg kg^{-1}, and Nd 105–478 mg kg^{-1}.

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Introduction

Rare earth elements (REE) are key materials for industries, playing crucial roles in the catalytic and metallurgical process, as well as the production of batteries, magnets, LED screens, and lasers. Thereby, their global production has increased exponentially in the past few decades, driving research towards alternative ways to explore and extract them (Redling 2006). REE encompass 17 elements, including all 15 lanthanides in addition to scandium (Sc) and yttrium (Y), and are usually divided into light (LREE) and heavy (HREE) groups, based on their atomic numbers. The LREE comprise the eight first elements of the lanthanides family, i.e. from lanthanum (La) to gadolinium (Gd), whereas HREE range from terbium (Tb) to lutetium (Lu) (Damhus et al. 2005).

The REE elements are mostly found in the trivalent oxidation state on granites, pegmatites, gneisses, and other forms of rocks (Hu et al. 2006; Tyler 2004). Although classified as "rare", these elements are more abundant than gold and other trace metals, e.g. copper (Hu et al. 2006). The approximate sum concentration of REE in the earth's crust ranges from 130 to 240 ug g^{-1}, but mineable concentrations are less common, making reserves potentially more valuable and strategic (Balaram 2019). Lide (1997) estimated that the most frequently available on earth's crust are Ce (66.5 ug g^{-1}), Nd (41.5 ug g^{-1}), La (39 ug g^{-1}), Pr (9.2 ug g^{-1}), and Sm (7.05 ug g^{-1}). Globally, China stands out with the largest REE reserves (38%), followed by Vietnam (18%), Brazil and Russia (17% each), and India (6%) (USGS, 2021).

Given high REE demand, there are increasing concerns about the REE-triggered environmental issues, e.g. their accumulation in plant tissues and the resulting entry into the food chain (Liu et al. 2018). Previous studies indicated that even nanomolar La concentrations were found to be toxic for the freshwater microalga *Desmodesmus* (Ashraf et al. 2021), as well as to animals (Hirano and Suzuki 1996). Interestingly, LaCl$_3$ and GdCl$_3$ are also reported to induce phosphate precipitation, thereby affecting nutrient availability and the radicular development of *Arabidopsis thaliana* seedlings in growth medium (Ruíz-Herrera et al. 2012). Nonetheless, there are few studies on this topic, and the lack of ecotoxicological data hinders the environmental risk assessment of REE for the determination of environmental thresholds (Gonzalez et al. 2014).

In this context, some plant species have the ability to hyperaccumulate REE. Despite the several definitions proposed, hyperaccumulators are generally classified as plant species with an increased tendency of metal sequestration in their tissues with no toxicity effects (van der Ent et al. 2013; Deng et al. 2018; Liu et al. 2018; Keeran et al.

2021; He et al. 2012). In this scenario, around 22 plant species have been identified either as potential partially REE accumulators or hyperaccumulators (Liu et al. 2018)., e.g. *Carya cathayensis* Sarg., *Dicranopteris dichotoma* (Thunb.) Bernh., *Dicranopteris linearis* (Burm. F.), and *Cyperus rotundus* L. (Robinson 1943; Chen et al. 2016; Wang et al. 2003; Khan et al. 2016).

In this scenario, hyperaccumulator REE species might serve as potential cost-effective and environmentally friendly models for phytomining and phytoextraction techniques of polluted soils and aquatic systems. Although the mechanisms related to REE uptake from soils are still not fully understood (Kastori et al.2010; Wyttenbach et al. 1994; Ye et al. 2008; Shan et al. 2003), it is mainly affected by REE bioavailability in soils, which, in turn, depends on many factors, including total soil REE content, type of soil, pH, organic matter composition, layer, and composition of the parent material (Fu et al. 2001). Since these characteristics vary across locations, achieving a proper phytoextraction approach requires a proper understanding of metals from soil to above-ground parts of hyperaccumulator plants.

Therefore, the present study investigated the spatial distribution and plant uptake of REE in a potential mining area located at Poços de Caldas municipality, Minas Gerais state, Brazil. We aimed at (i) prospecting plant species able to hyperaccumulate LREE, which could be candidates for phytomining and (ii) gaining insight into the bioavailability of LREE for plant uptake. Thus, in addition to screening plant species in the area, we evaluated the total and extractable content of LREE in soil.

Materials and methods

Soil and plant collection

The soils and plants were collected in an area of 5500 m^2, where there is a 5–6-year-old commercial *Eucalyptus* forest in Poços de Caldas municipality, Minas Gerais State, Brazil. The area consisted of a thorogummite and bastnaesite bearing REE deposit in which mining activities are planned (Takehara 2015). In such a context, the site has been previously characterized by light slope and exhibited a 70 m long, 2 m wide, and 3 m deep trench (Fig. S1).

In April 2019, a first survey was carried out including 31 soil composite samples (0–20 cm depth). Each sampling spot, located at *ca*. 10 m distance from each other, consisted of three to four soil subsamples collected within a 1-m interval using shovel and hoes and then gathered and mixed in plastic bags. The soil samples collected within the trench were labelled by the letter T (T1–T7), whereas the others were named in reference to this trench, i.e. either "above the trench", A, "below the trench", B, or "surrounding the

trench", M. Each sampling spot was geo-referenced using a UTM (Universal Transverse Mercator) app (GeoMap, Y2 Technology, Indonesia). The soil was classified as Oxisol, and the pH was determined by a benchtop pH-meter (Tecnal, TEC-2, Brazil) using a 1:1 ratio water-soil mixture, as described by Sparks et al. (1996).

Moreover, at least three plant specimens were collected in *ca.* 4 m^2 areas surrounding each soil sampling spot, including some from the *Eucalyptus* spp. commercially explored in the area. This first plant screening was aimed at identifying promising LREE accumulating specimens (La, Ce, Pr, Sm, and Nd). The plant samples were stowed in paper bags and then identified at the family level using a botanical key from Souza and Lorenzi (2014) as multiple individuals within *Solanaceae, Lamiaceae, Adoxaceae, Cornaceae, Rosaceae, Melastomataceae, Lauraceae, Myrtaceae, Thelypteridaceae, Moraceae*, and *Poaceae* families. For some specimens, it was possible to collect the whole plant, while for others only leaves. Initially, the plants were identified at the family level using a botanical key from Souza and Lorenzi (2014), and some eucalyptus species commercially explored in the area were also collected.

In December 2020, a second field collection was targeted at sampling potential LREE accumulators or hyperaccumulators families based on 2019 processed plant specimens. This included individuals within the *Lamiaceae, Melastomataceae, Thelypteridaceae*, and *Poaceae* families. The most promising specimen in terms of LREE accumulation capacity was identified at the species level by a professional systematic botanist as *Christella dentata* (Forssk.) Brownsey & Jermy, and the collected specimens were deposited at the E.S.A. Herbarium of the Luiz de Queiroz College of Agriculture of the University of São Paulo, in Piracicaba municipality, Brazil (specimen codes ESA144468, ESA144469, and ESA144470). All samples were then air-dried and manually ground using liquid nitrogen for further analysis.

Sample preparation for LREE determination

The quantification of the total LREE content (La, Ce, Sm, Pr, and Nd) in the soil samples was carried out by wavelength dispersive X-ray fluorescence (WDXRF, S8 Tiger, Bruker AXS, Germany). The samples were dried in a laboratory oven at 60 °C to constant weight, ground in a ball mill, and passed through a 100-mesh sieve. Then, 3 g of sample and 7 g of boric acid were weighted and used for preparing the pellets. The boric acid was used as the bottom of the pellets.

Besides, the extractable contents of LREE were determined by inductively coupled plasma mass spectrometry (ICP-MS) aiming at determining the fraction that emulates plant-available REE, i.e. those involved in water-soluble, exchangeable fractions, and the weakly bound carbonates phase (Quevauviller et al. 1997). For that, 15 mL of 0.1 mol L^{-1} acetic acid was added to 0.5 g of dried and homogenized soil and continuously shaken at room temperature for 16 h. The mixture was ultracentrifuged for 20 min at 14,336 g at room temperature. The supernatants were separated and filtered with syringes containing 0.45 µm pore size filters, and the solution was transferred to decontaminated vials.

Plant samples were divided into roots and shoots. Due to the low root dry mass obtained for most of the collected specimens, only shoots were used for the determination of REE content. The shoots were thoroughly washed with deionized water and subsequently dried at 60 °C for 48 h. The dried tissues were manually milled using a crucible and liquid nitrogen, and 0.250 g of ground samples were transferred to decontaminated Teflon® tubes. Then, a mixture of 6 mL of 20% (v/v) sub-boiling distilled nitric acid and 2 mL of 30% (v/v) H_2O_2 were used for the digestion. The tubes were closed and placed in a single reaction chamber with microwave-assisted heating. The system was closed and pressurized with Ar at 40 bar; Table S1 of ESI indicates the information for the heating program. Thereafter, digested sample solutions were transferred to 50 mL falcon tubes, and the volumes were completed to 15 mL with ultrapure water.

Quantification of REE

For the WDXRF, the quantification was performed using soil-based external calibration curves, which had been prepared using stock solutions of lanthanides standards. The limit of detection (LOD) for the WDXRF was determined according to Equation S1. The Recoveries for La, Sm, Ce, Nd, and Pr were evaluated using two soil samples spiked with 5,000 mg kg^{-1} of these REE, the method returned recovery values ranging from 72 to 107%.

For the ICP-MS analyses of both soil and plant tissues, multielement standards were prepared by appropriate dilutions of multi-elemental reference standards containing light rare earth elements (La, Ce, Pr, Sm, and Nd). The conditions for determination were optimized, and terbium (Tb) was used as an internal standard. Soil analysis was performed only once, with each extracted sample having been measured twice by ICP-MS. Values were averaged together, and the results were presented. Plant tissue analysis was performed in duplication, and the results represent the average values. The limits of detection and quantification for ICP-MS were calculated as three and ten times the standard deviation of the blank samples, respectively, divided by the slope of the calibration curves (0–200 µg L^{-1}). The analytical parameters obtained for the calibration of each element for WDXRF and ICP-MS are presented in Tables S2 and S3. The accuracy of the ICP-MS analysis was checked by analysing the LREE content in standard reference material (Bush leaves and branches) GBW07603 and (Tomato leaves) SRM 1573a. Percentage recoveries were calculated

for validation of instrumental procedures. The recoveries are shown in Table S4 of ESI for each determined LREE (La, Ce, Nd, Pr, and Sm) in SRM (Standard Reference Material).

Statistical analysis

Statistical regression analysis at the level of 5% was performed for significant variation ($p < 0.05$), to determine the correlation between the total content of most LREE (La, Ce, Nd, Pr, and Sm) (g kg^{-1}) with extractable contents in soils (mg kg^{-1}), and with plant concentration (mg kg^{-1}) to assess plant availability. ANOVA-linear regression model (R^2) was used in that case for the correlation of each determined element. Statistics were performed using Excel (version, 2010, Microsoft Co., USA). The means, median, and standard deviations of data were calculated and presented. All figures were completed using OriginLab (Version 2019, OriginLab Co., USA).

Results and discussion

Total LREE concentrations in soil samples

Figure 1 shows interpolated maps revealing the total concentration (g kg^{-1} dry soil) and spatial distribution patterns of REE in the area. The results are also presented in Table S5 of the ESI. All the data were analysed by ANOVA linear regression, which indicated that all determined LREE (particularly most abundant; La, Ce, Nd, Sm, and Pr) are not homogeneously distributed. As a result, we employed a geometric mean for all individual LREE determined in a mining region to describe the average concentrations. Our results indicate that sample A9, which was taken above the trench, was the hotspot for Ce and Sm, while the trench was a hotspot for Pr, La, Sm, and Nd. Out of a few exceptions, Ce was the most abundant LREE in the sampling spots. The degree of dispersion is also expressed by the coefficient of variation, a low coefficient indicating more homogenous distribution, while a high coefficient of variation indicates spatially non-homogeneous distribution or high dispersion of rare earth elements in the studied area. The coefficients of variation for Pr and Nd were the highest and lowest, respectively. The total sum concentration of tested LREE in 31 soil samples reported by the present study varied from 6 up to 38 g kg^{-1} and the average total concentration of individual LREE was 7.7 ± 5.3 g kg^{-1} for Ce, 3.4 ± 3.0 g kg^{-1} for La, 0.4 ± 0.3 g kg^{-1} for Sm, 2.1 ± 1.2 g kg^{-1} for Nd, and 0.6 ± 0.5 g kg^{-1} for Pr. Previous studies performed in Australia and Germany found that REE varied from 32 to 194 mg kg^{-1} and 42 to 544 mg kg^{-1}, respectively (Diatloff et al. 1996; Loell et al. 2011).

Similarly, to the results found at Bayan Obo, China, our results displayed higher LREE contents as compared to HREE, with Ce being highest, then La and so on among all REE in fluorite deposits, thus following the trend, i.e. Ce > La > Nd > Pr > Sm (Xu et al. 2012). Such a trend, known as the Oddo-Harkins rule, i.e. Ce > La > Nd > Pr > Sm (Zhenggui et al. 2001), was also reported by Taylor and McLennan (1995) as the elemental composition of the continental crust. According to this rule, Ce is highest in the upper crust (64 ppm) followed by La (30 ppm), Nd (26 ppm), Pr (7.1 ppm), and Sm (4.5 ppm). It indicates that the content of individual LREE decreases with increasing atomic numbers and those elements with even atomic numbers are more abundant in the earth's crust than those with odd numbers (Wang et al. 2014; Laveuf and Cornu 2009).

One should notice that the total concentration of REE in soil depends on the type and composition of parent material, the landscape, and the geochemical age of the location. The usual concentration of REE in parent material varies from 0.1 to 100 mg kg^{-1} (Aide and Aide 2012). Reimann et al. (2018) surveyed soil samples across Europe employing a modified *aqua regia* dissolution method and reported that the median concentration of Ce and La was 28.4 mg kg^{-1} and 14 mg kg^{-1}, respectively. Moreover, Wang and Liang (2015) investigated the concentration of REE in Chinese mining tailing trough the HNO$_3$-HF-HClO$_4$ digestion method and found that the values ranged from 0.156 to 57 g kg^{-1} with an average value of 4.67 g kg^{-1}. The total concentration reported by the present study was higher than the values reported in mining sites in Poland (Karczewska et al. 2019), which exhibited maximum concentrations of Ce, La, Nd, Pr, and Sm of 185, 108, 110, 27, and 26 mg kg^{-1}, respectively. In the present study, the median concentrations for Ce, La, Nd, Pr, and Sm were 5.2, 2.4, 1.7, 0.4, and 0.3 g kg^{-1}, respectively.

In principle, the concentrations reported in the present study could be damaging to soil biota and plant growth (von Tucher and Schmidhalters 2005). Relatively low concentrations of REE can exert toxic effects on the overall growth and photosynthesis in aquatic microorganisms (Ashraf et al. 2021) and terrestrial plants (Ruíz-Herrera et al. 2012). However, in the present study, plants grown in excess of total REE did not show signs of detrimental effects; this could be explained by the low extractability of these elements by roots.

Extractable LREE in soils

Figure 2 shows an interpolated map displaying the concentration of extractable LREE. In addition, Table S6 in the ESI presents the values found for each extracted soil sample. The plant-available content indicates that the samples collected in the middle and inside the trench were the hotspots for all determined lanthanides, except Ce, which was
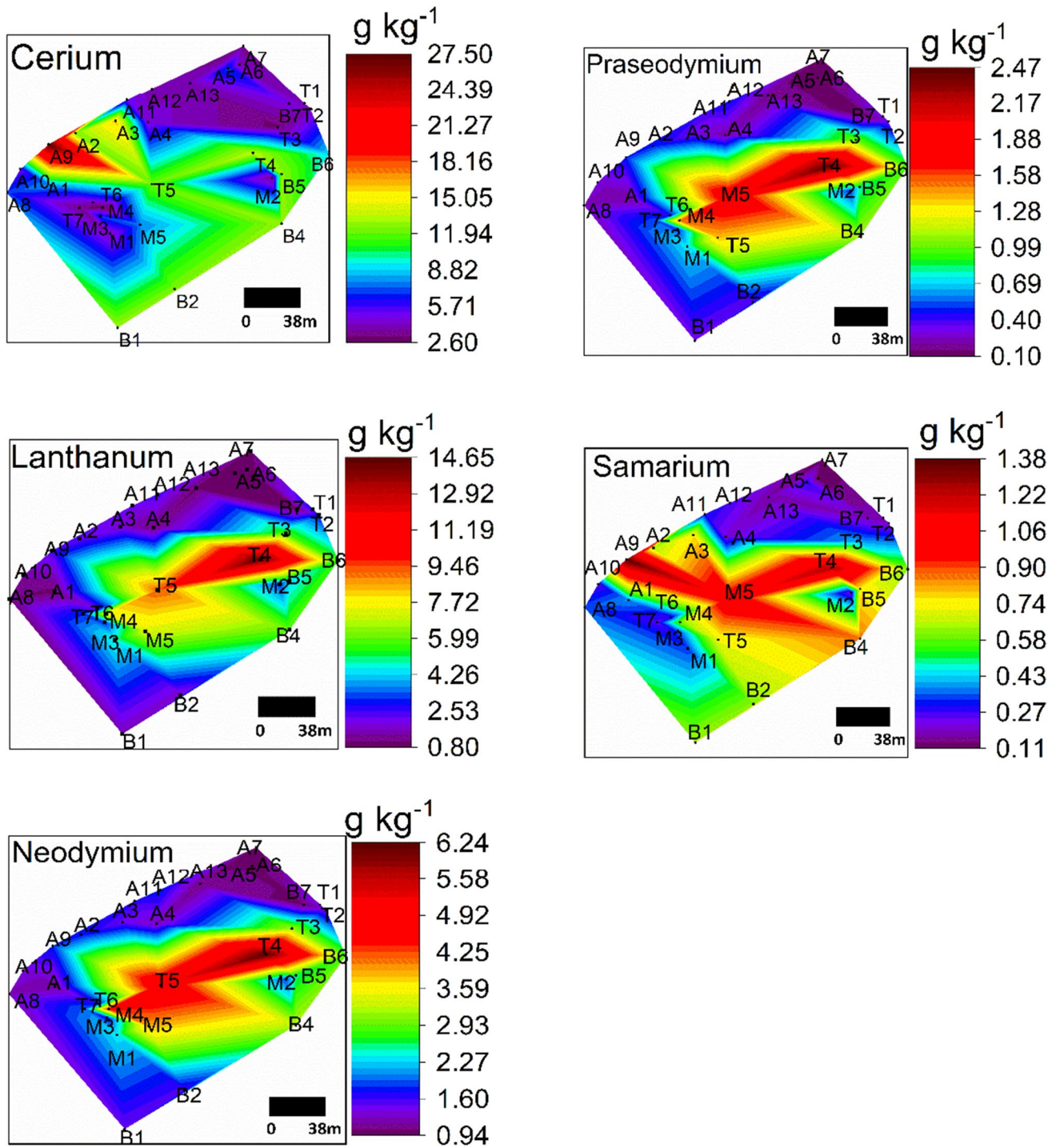
Fig. 1 Colour maps represent the distribution of total LREE content determined by WDXRF in the soil collected from the spots. A, indicates above; T, inside the trench; M, middle; and B, below the trench. Red to violet: high to low concentration in g kg^{-1} dry matter
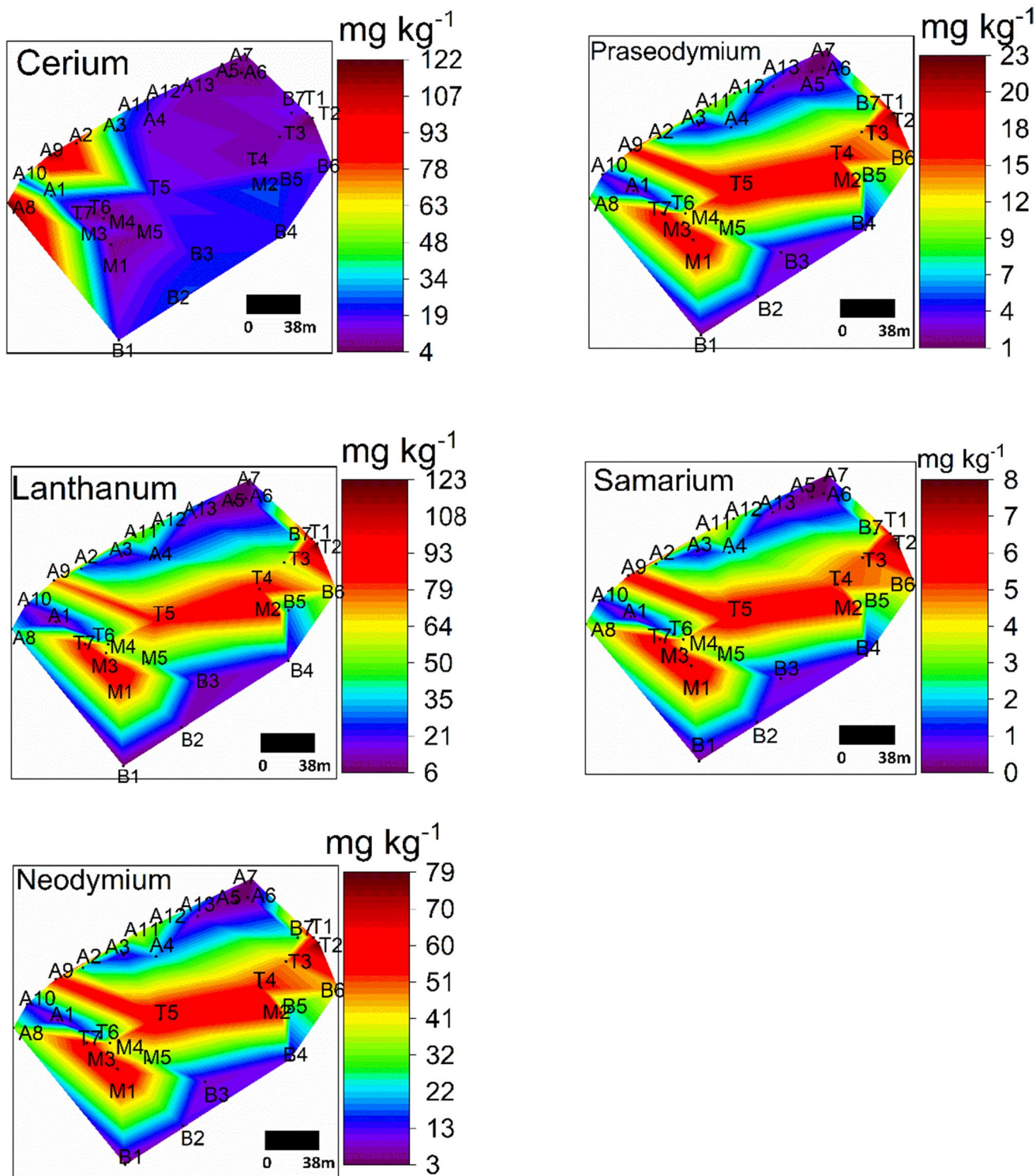
Available Lanthanides Content mg/kg

Fig. 2 Colour maps represent the prospection of available LREE content determined by ICP-MS in the soil collected from the spots. A, indicates above; T, inside the trench; M, middle; and B, below the trench. Red to violet: high to low concentration in mg kg^{-1} dry matter

mostly localized above the trench (samples A2, A8, and A9, respectively).

The procedure employed to determine the concentration of REE in the extracts was proposed by the Community Bureau of Reference (BCR) (Li et al. 1998). It has been mainly employed to determine the mobility of elements in soils and plant uptake via roots (Mittermüller et al. 2016). In the present study, it aimed at mimicking the LREE available for plants. According to our results, the average LREE content obtained in the first step of the sequential procedure revealed that REE bound to the water-soluble, exchangeable, and carbonates bound was in the range between 0.58 and 1.05% of total LREE in soil. The fraction of extractable LREE found in the present study is shown in Fig. S2, with an average of $1.27 \pm 1.1\%$ and a median fraction of 0.95%. These values agree with those previously reported by Li et al. (1998). The average values of the individual tested LREE in our present study were 45 ± 37 mg kg^{-1} for La, 24 ± 17 mg kg^{-1} for Ce, 3.2 ± 3.0 mg kg^{-1} for Sm, 32 ± 30 mg kg^{-1} for Nd, and 9.0 ± 8.3 mg kg^{-1} for Pr.

Figure 3 shows positive correlation between total (g kg^{-1}) and extractable (mg kg^{-1}) LREE. Pearson's correlation coefficients were 0.59 for Ce, 0.57 for La, 0.55 for Pr, and 0.53 for Nd with $p < 0.05$; the lowest value was found for Sm 0.05, which was not significant. The dissolution of REE is likely a complicated process, which depends on other factors in addition to the total concentration. The slopes of the adjusted curves suggest that REE are not equally available. Keeping in mind the low coefficient of determination, Ce is the most available, while Sm is the least. Therefore, the distinct bioavailability of each LREE suggests that this parameter depends on intricate phenomena in the rhizosphere. REE
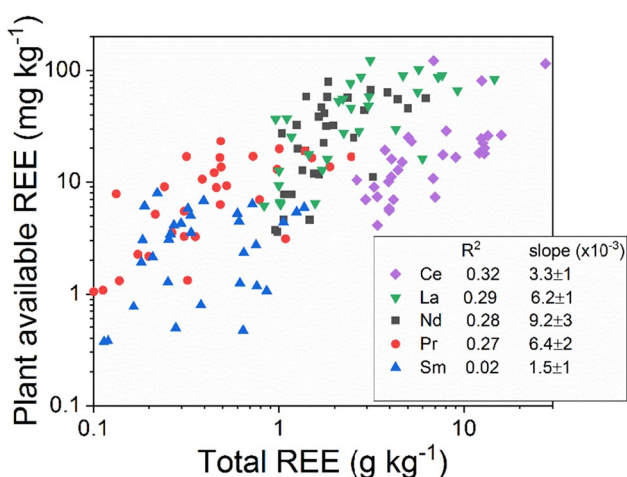

Fig. 3 Scatter plot depicting the relation between plant available LREE (mg kg^{-1}) versus total LREE (g kg^{-1}) in soil, for each element. The significance level for each correlation was calculated at a 5% level for each element

speciation could also be one of the important factors that lead to different bioavailability ratios for each lanthanide.

The first fractionation step extracts water-soluble and exchangeable forms of lanthanides (Bruemmer et al. 1986; Petruzzelli 1989). As mobilization of bound REE from soils is highly effective under an acidic environment, extraction by the acetic acid method under low pH was found to be effective to mimic the REE availability for plants. Thus, in the future, full fractionation could give more effective extraction for bound oxides, phosphates, sulphides, and organic matter associated with soils. REE were bound to carbonates, which correspond to the main mineral present in the studied area and are hardly available to plants (Viets 1962). Xian and Shokohifard (1989) proposed that metals bound to carbonates in soils can be mobilized when the pH of the soil is low enough to dissolve their carbonates. The acidification of the rhizosphere can be accomplished by plant exudates and by microorganisms living in the root phyllosphere (Qu et al. 1995).

Bioavailability is a critical process, affected by many factors that illustrate the amount of metals concentrated by the plants. For example, in a study conducted in Xinfeng, southern Jiangxi Province, the proportion of extractable content accounted for 14.9% of the total content in tailings, using the Tessier extraction procedure (Wen et al. 2013). The high bioavailability could be explained by the fact that these regions have a large volume of REEs tailings and have the potential for phytomining using REE hyperaccumulators (Guo et al. 2014). The present results are consistent with the data published in Mittermüller et al. (2016), which explain the extraction procedure to evaluate the mobilization of REE in solid materials, including soils and tailings. They found that Ce was the most abundant bioavailable LREE corresponding to 37–40% of the total. In our results, we found La as the most abundant bioavailable, while Sm was the least. The lower bioavailability of Sm in the present study, i.e. 3 mg kg^{-1}, compared to other determined LREE, is a consequence of the difficult mobilization behaviour of Sm from soils. Cao et al. (2000) performed a sequential extraction method to study REE bioavailability among normal soils that are not fertilized and concluded that exchangeable REE fractions that lead to bioavailability gradually decreased for Sm and others with time as they were slowly bound to soil particles. Hardly mobile metals like Sm represent a lower risk to living biota compared to easily soluble fractions because negatively charged groups in soil organic matter can chelate cations like REE (Fiket et al. 2017) and thereby decrease their availability and transfer to plants.

In the present study, soil pH out and within the trench was 4.2 and 5.2, respectively. Mobilization of lanthanides mainly increases with the decrease in pH of the soil as REE concentrations in soil solutions are inversely correlated with pH (Cao et al. 2001). However, availability is a rather complex

phenomenon that is not only dominated by pH or total concentration. Other soil properties, such as texture and biotic factors, can explain REE availability.

Determination of LREE in plant specimens

As shown in Fig. 4, 54 plant specimens from 11 families were collected during the first screening campaign in 2019. The LREE concentration in the shoots of each plant sample is presented in Table S7. The concentration values for tested LREE ranged from 0.01 up to 7 mg kg^{-1}, presenting median concentration for La, Ce, Pr, Nd, and Sm of 6.5, 6.9, 0.7, 2.4, and 0.2 (mg kg^{-1}) among shoots, respectively. Figure S3 does not show any significant ($p > 0.05$) correlation between the concentration of LREE in the extracts and plant tissue.

The concentrations of LREE found in this first campaign were lower than those reported by Wang et al. (1997); in particular, they reported that the fern *D. dichotoma* presented concentrations of all REE in the range of 675–3360 mg kg^{-1} on average. One can note in Table S7 that the concentration levels of REE that were found in the *Thelypteridaceae* ferns were consistently higher than those found in other botanical families. The values found by the present study are comparable to those reported by Grosjean et al. (2020) in ferns, who reported LRRE below 10 mg kg^{-1} on average.

Among the plants collected during the second campaign (2020), the most remarkable was *Christella dentata* (Forssk.) Brownsey & Jermy, a native rupicolous fern belonging to the *Thelypteridaceae* family mainly found at riverine, seasonally semideciduous, and ombrophyllous forests across the whole country (Salino et al. 2020). This species exhibited the highest concentration of tested LREE, and the concentration of each determined LREE in our present study varied among the individuals. We found La concentrations ranging from 190 up to 703 mg kg^{-1}, Ce from 115 up to 1872 mg kg^{-1}, Pr from 32 up to 144 mg kg^{-1}, Nd from 105 up to 478 mg kg^{-1}, and Sm from 9.1 up to 48 mg kg^{-1} in 6 individuals (Fig. 5).

The detailed values are given in Table S8 of ESI. Assuming that the concentrations of LREE present a normal distribution in the *C. dentata* population, the Dixon test indicates that the individual number 3 is an outlier; hence excluding it, the average concentration of individual LREE tested in *C. dentata* was 281 ± 115 mg kg^{-1} for La, 232 ± 110 mg kg^{-1} for Ce, 48 ± 21 mg kg^{-1} for Pr, 162 ± 74 mg kg^{-1} for Nd, and 15 ± 7 mg kg^{-1} for Sm. Due to the apparent tolerance of *C. dentata* towards LREE and the elevated concentration of LREE in its shoot, it may consist of good material to study the biochemical functions and the long-term biological effects of REE on plants and therefore considered as the preferential accumulator of LREE during the soil to shoot assimilation. Despite the suggested threshold concentration of 1000 µg g^{-1} for defining as species a hyperaccumulator, which is the same used for other elements such as copper and nickel (Garbisu et al. 2001), this first survey suggested *C. dentata* as a potential hyperaccumulator for LREE. Previous studies on the capacity of *C. dentata* accumulating elements other than LREE revealed that it toke up arsenic from contaminated soils and stored it in both roots and shoots with the concentration in leaves was 40.3 mg kg^{-1} (Raj et al. 2015).

To date, nearly 500 hyperaccumulator plant species have been identified from 45 different families (Mathew et al. 2022), and the majority of them are for heavy metals like nickel and chromium. Hyperaccumulation in plant species shows wide variations for metal uptake, even confined under metalline soils; this reflects the extreme variations in concentrations available in extractable forms in soils, normally depend on fluctuations in soil pH and other properties (Reeves et al. 2017). For lanthanides hyperaccumulation, mostly fern species have been reported that can concentrate higher quantities of LREE (mainly, La and Ce); for example, Ozaki et al. (2000) reported many Pteridophytes as hyperaccumulators of LREE. In this context, a study conducted in a former mining area in Malaysia appoints *D. dichotoma*, *D.*

Fig. 4 Distribution of the plant families collected in 2019 at Poços de Caldas city, Brazil. A total of 54 plant specimen were collected from 11 respective families, as well as their percentiles related to the total samples are reported
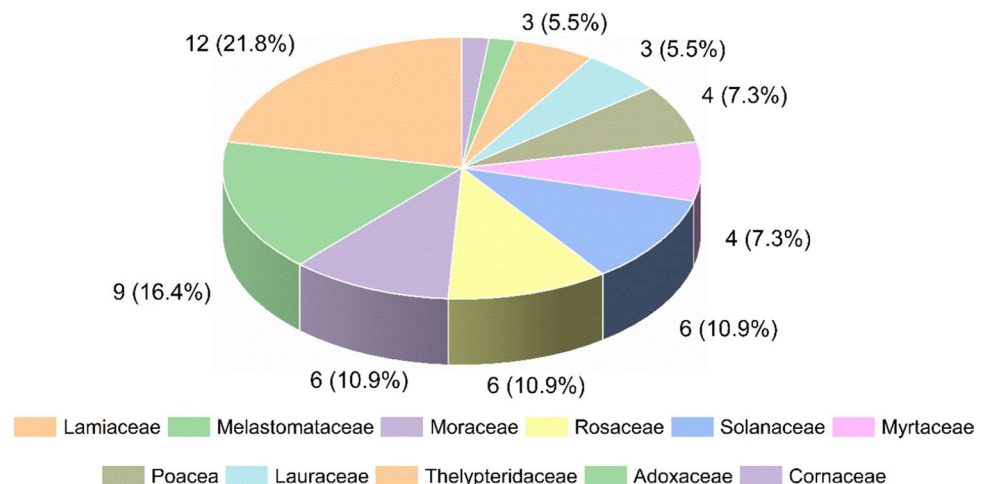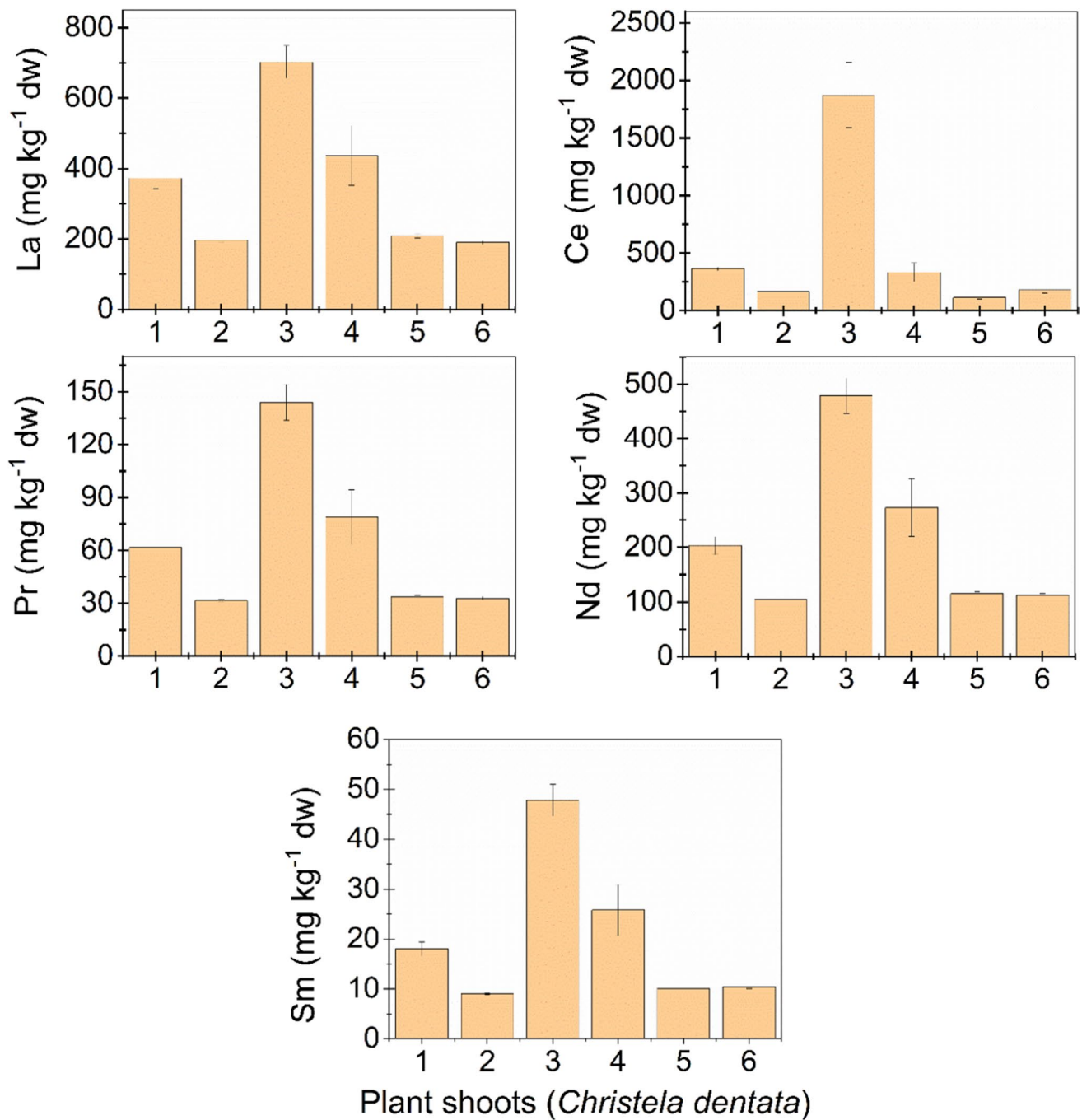
Fig. 5 Light Rare earth elements (LREE) content in mg kg^{-1} determined by ICP-MS in the shoots of the plant species *Christella dentata* in the studied area. The *X*-axis represents total individuals collected from respective species, and the *Y*-axis represents the concentration in mg kg^{-1} of dry matter

linearis, and *C. rotundus* as hyperaccumulator species for REE, especially for Ce, whose concentrations in the shoots were consistently higher compared to other LREE, reaching 738 mg kg^{-1}, 707 mg kg^{-1}, and 340 mg kg^{-1}, respectively, in each of the mentioned species (Khan et al. 2016). Such values are in the same order of magnitude as those reported for Ce in *C. dentata* in the present study. In China, the ΣREE

(sum concentration) found in *D. dichotoma*, another well-known LREE accumulator fern, was 3,358 mg kg^{-1} among shoots collected in a mining area of Ganzhou Jiangxi province (Wang et al. 1997), although the high variability in these concentrations among the sampling sites also exists. Besides, lower Ce concentrations were previously reported (Wang et al. 2003) among leaves of *D. dichotoma*, as

compared to our reported species, *C. dentata*, which indicates its strong capacity to accumulate and transport Ce. Studies on REE hyperaccumulation suggest that until now 22 REE hyperaccumulator plant species have been identified (Liu et al. 2018). They belong to 11 plant families, with a high number of ferns, for example, the well-known *Phytolacca americana* L. that exhibited good accumulation capacity for both light and heavy REE among shoots. However, the concentration varies among sampling sites; it is known that it can accumulate up to 623 μg g^{-1} of REE in dry leaves (Ichihashi et al. 1992), and in an REE mining site in the south of Jiangxi Province, *P. americana* accumulated up to 1,012 μg g^{-1} in leaves (Liu et al. 2018).

Conclusion

The extractable LREE (La, Ce, Pr, Nd, Sm), which proxies the plant-available LREE concentrations, represented a fraction of nearly 1 wt.% of total bioavailable LREE. The spatial correlation between the total LREE concentrations and the plant-available ones showed that availability is a rather complex phenomenon, which was not only dominated by concentration but other physical–chemical characteristics of the soil. Furthermore, the lack of significant correlation between the total concentration of tested LREE and the concentrations found in plants suggests that the uptake of LREE or hyperaccumulation by plants from contaminated soils is dependent on concentrations available in extractable forms in soils that plants can concentrate in their living tissues; thus, uptake mechanisms via roots are not only controlled by diffusion or mass flow mechanisms. It likely also involves intricate molecular mechanisms. Further studies are required to increase the accuracy of extraction methods to mimic roots for plant uptake capacity and its localization to understand the long-term effects of lanthanides and possible uptake mechanisms. Some plants like the fern *Christella dentata* have been found as a potential hyperaccumulator for LREE and thus have the potential for LREE phytomining. Future studies shall be carried out with *C. dentata to* evaluate which tissues and what is the chemical form (redox states and ligands) of the accumulated LREE. Besides that, studies are needed to employ a combination of plant physiological, molecular biological, and geochemical tools to better understand specific mechanisms of REE fractionation and accumulation in plants grown in polluted regions.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Competing interest The authors declare no competing interests.

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