

## POTENTIAL FOR PHYTOMINING OF RARE EARTH ELEMENTS BY NATURALLY OCCURRING PLANTS IN RECLAIMED TAILING PONDS

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### Abstract

Rare earth elements (REEs) from the ex-mining area (reclaimed tailing ponds) in East Rodope, Bulgaria, were investigated in soil and different plant species using inductively coupled plasma-optical emission spectrometry (ICP-OES). The tailings pond was reclaimed 20 years ago. The research work aims to determine the potential for phytomining of rare earth elements by naturally occurring plants in reclaimed tailing ponds. In the soil samples, the concentrations of cerium (Ce), lanthanum (La), and gadolinium (Gd) exceeded the average content of the elements in soils. The bioconcentration factor (BCF) was calculated. It was found that light rare earth elements (LREEs) are in greater concentration in plant samples than heavy rare earth elements (HREEs).

**Keywords:** Rare earth elements; Tailing Pond; Bioadsorption

### Introduction

The rare earth elements (REEs) are becoming more and more significant in industry, particularly in environmentally friendly high-tech products like wind turbines, hybrid and electric vehicles, batteries, and even in agriculture as fertilisers [1]. REEs include Sc, Y, and the 15 lanthanoides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). Rare earth elements are not uncommon. They have an average abundance of 66mg.kg<sup>-1</sup> for Ce and 0.1mg.kg<sup>-1</sup> for Pm [1]. The most common rare earth element, cerium (Ce), has a concentration that exceeds that of common metals like lead (14.0mg.kg<sup>-1</sup>) and copper (60.0mg.kg<sup>-1</sup>). The total content of REE varies in the following order: Ce > La = Y > Sc > Nd > Sm > Pr > Gd > Dy > Eu > Tb > Er > Yb > Ho > Lu > Tm [2].

Its content varies with soil characteristics such as mineralogy, soil texture (the clay content), pH, and organic matter content [3–5]. Rare earth elements are typically dispersed due to their geochemical characteristics. This indicates that they are not frequently discovered in sufficiently concentrated clusters to be mineable. Therefore, the recovery of REEs from secondary resources and the remediation of REE contamination [3] are urgent challenges that have recently drawn more attention.

Phytomining is an innovative technology for extracting REEs from materials that conventional mining is ineffective or unprofitable at extracting. In recent years, this method for recovering noble metals has been introduced in its entirety. Despite this, very little attention has been paid to the technology or potential of REE phytomining. Native plants, which are widespread geographically, are of special importance from this perspective since they are

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genetically adapted to contamination and can either remove or retain it, lowering its toxicity in soil. They could belong to a group known as hyperaccumulators, a class of plants that can tolerate, absorb, accumulate, and translocate high levels of metal(loid)s, or excluder plants, which may retain relatively low levels in their shoots while still having significant quantities of metal(loid)s in their roots. Numerous studies [6–8] have also demonstrated that native plants grown in contaminated areas are more resistant due to higher disposal efficiency. They also have more metal accumulation and resistance to environmental stresses than plants grown in non-contaminated areas [9].

The study was conducted to determine whether native plant species are suitable for phytomining of rare earth elements in a reclaimed tailings pond (Eastern Rhodopes, Bulgaria).

## Experimental part

### *Study area*

This investigation focuses on a reclaimed tailings pond in the Eastern Rhodopes. The tailings pond is formed by lead-zinc ore extraction. It was reclaimed 20 years ago. The tailings pond is reclaimed by the grassing of the tailing beach, slopes, and bermes and the afforestation of slopes with deciduous shrubs.

### *Materials*

For the analysis, two tailings' samples (TS1 and TS2) and three mixed soil samples (SS1, SS2, and SS3) were taken from the tailings pond. In compliance with ISO 18400-105:2019 (Soil quality – Sampling), sampling was done. The following plant species' leaf masses were sampled from the established vegetation in the field: *Euphorbia niciciana*, *Lolium perenne*, *Verbascum densiflorum*, *Cichorium intybus*, *Salix alba*, *Alnus glutinosa*, *Morus alba*, and *Betula pendula*. The samples were taken at the end of the growth season (in October).

### *Methods*

Soil acidity is determined by a potentiometric method. The total acid dissolution procedure was applied to all samples (soils and plants). The amount of REEs (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Sc, Sm, Tb, Y, and Yb) was determined by inductively coupled plasma optical emission spectroscopy (ISP-OES).

In this study, the contamination factor (CF) was used for the assessment of soil contamination according to the relationship:

$$\text{CF} = \text{REEs concentration in soil} / \text{REEs reference value} \quad (1)$$

If  $\text{CF} < 1$ , soil quality is classified as low contamination,  $1 \leq \text{CF} < 3$  as moderate contamination,  $3 \leq \text{CF} < 6$  as considerable contamination, and  $6 \leq \text{CF}$  as very high contamination. In this study, we examined the concentration of elements in the earth's crust. Maximum permissible concentrations are usually used as a divisor. Regarding REEs, however, they are not regulated because their toxicity to plants is less than that of heavy metals. As a result of their low solubility and mobility in soils, REEs have historically been viewed as having little risk to the environment or human health.

To evaluate native plants in study areas for their ability to extract REEs from soil, the bioaccumulation factor (BCF) of shoots was calculated:

$$\text{BCF}_{\text{shoot}} = \text{REEs concentration in leaf} / \text{REEs concentration in soil} \quad (2)$$

It was suggested that plants exhibiting greater than 1 BCF leaf have the potential to be used for phytoextraction [10, 11].

**Results and discussion**

***Heavy metal and metalloid content***

The contents of the studied rare earth elements in soil (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Sc, Sm, Tb, Y, and Yb) are presented in Table 1.

**Table 1.** REEs content in soil and tailings samples and abundance in the Earth's crust

Sample	pH	Ce	Dy	Er	Eu	Gd	Ho	La	Lu	Nd	Sm	Sc	Tb	Y	Yb
	-	mg.kg <sup>-1</sup>													
SS1	7.0	95.4	4.2	2.6	2.0	9.5	1.0	47.9	0.3	38.5	6.1	14.3	1.1	28.2	2.3
SS2	6.1	78.1	3.7	2.1	1.6	7.3	0.8	37.2	0.3	29.1	5.9	12.7	0.8	20.7	1.8
SS3	5.7	56.6	2.9	2.0	1.5	5.1	0.6	27.7	0.2	22.0	5.0	11.7	0.7	18.0	1.7
TS1	4.2	32.0	1.5	1.1	1.1	3.3	0.5	16.5	0.2	12.8	2.3	6.2	0.3	11.1	1.1
TS2	4.1	29.2	1.4	1.1	1.0	2.7	0.3	15.5	0.1	11.9	1.9	6.7	0.3	9.5	1.0
Abundance		66.5	5.2	3.5	2.0	6.2	1.3	39.0	0.5	41.5	7.0	22.0	1.2	33.0	3.2
Subsoil		54	3.6	2.18	0.8	4.2	0.7	25.6	0.31	22.4	4.4	9.2	0.64	23.0	2.1
<b>Topsoil</b>		<b>48</b>	<b>3.4</b>	<b>1.98</b>	<b>0.7</b>	<b>3.8</b>	<b>0.7</b>	<b>23.6</b>	<b>0.30</b>	<b>20.8</b>	<b>3.9</b>	<b>8.2</b>	<b>0.6</b>	<b>21.0</b>	<b>2.0</b>

There is a wide range of acidity in the soil samples, ranging from moderately acidic to neutral, and in the tailings, it is extremely acidic. These data suggest that REE extraction in the investigated samples is possible. It is known that the adsorption of REEs depends on pH and soil cationic exchange capacity (CEC), and the availability of elements increases with a decrease in pH and redox potential [11, 12].

All elements were present in the tested samples. Cerium concentration varies from 29.2 to 95.4mg.kg<sup>-1</sup>. In the soil samples, the element concentration was higher than the average element content in the topsoil (48.0mg.kg<sup>-1</sup>). The Ce concentration of tailings is below the abundance in the crust (66.5mg.kg<sup>-1</sup>). Dysponium concentration varies from 1.4-4.2mg.kg<sup>-1</sup>. The concentration of the element in soil is above the average value in topsoil – 3.4mg.kg<sup>-1</sup> in SS1 and SS2 [13]. The Dy concentration of tailings is below the abundance in the crust (5.2mg.kg<sup>-1</sup>). Erbium concentration varies from 1.1-2.6mg.kg<sup>-1</sup>. The concentration of the element in soil is above the average value in topsoil – 1.98mg.kg<sup>-1</sup>. The Er concentration of tailings is below the abundance in the crust (3.5mg.kg<sup>-1</sup>). Europium concentration varies from 1.0-2.0mg.kg<sup>-1</sup>. The concentration of the element in soil is above the average value in topsoil – 0.7mg.kg<sup>-1</sup> in all samples, inclusive of tailings. In terms of rarity, europium is one of the less abundant rare earth elements; it is almost as abundant as tin. There is no free form of this element in nature [13]. Gadolinium concentration varies from 2.7-9.5mg.kg<sup>-1</sup>. The concentration of the element in soil is above the average value in topsoil – 3.8mg.kg<sup>-1</sup>. The Gd concentration of tailings is below the abundance in the crust (6.2mg.kg<sup>-1</sup>). Holmium concentration varies from 0.3-1.0mg.kg<sup>-1</sup>. The concentration of the element in soil is above the average value in topsoil – 0.7mg.kg<sup>-1</sup>. The Ho concentration of tailings is below the abundance in the crust (1.3mg.kg<sup>-1</sup>). Lanthanum concentration varies from 15.5-47.9mg.kg<sup>-1</sup>. The concentration of the element in soil is above the average value in topsoil – 23.6mg.kg<sup>-1</sup>. The La concentration of tailings is below the abundance in the crust (39.0mg.kg<sup>-1</sup>). Lutetium concentration varies from 0.1-0.3mg.kg<sup>-1</sup>. The concentration of the element in soil is equal to the average value in topsoil: – 3.4mg.kg<sup>-1</sup> in SS1 and SS2. The Lu concentration of tailings is below the abundance in the crust (0.5mg.kg<sup>-1</sup>). Neodymium concentration varies from 11.9-38.5 mg.kg<sup>-1</sup>. The concentration of the element in soil is above the average value in topsoil – 20.8mg.kg<sup>-1</sup>. The Nd concentration of tailings is below the abundance in the crust (41.5mg.kg<sup>-1</sup>).

<sup>1</sup>). Samarium concentration varies from 1.9-6.1mg.kg<sup>-1</sup>. The concentration of the element in soil is above the average value in topsoil – 3.9mg.kg<sup>-1</sup>. The Sm concentration of tailings is below the abundance in the crust (7.0mg.kg<sup>-1</sup>). Scandium concentration varies from 6.7-14.3mg.kg<sup>-1</sup>. The concentration of the element in soil is above the average value in topsoil – 8.2mg.kg<sup>-1</sup>. The Sc concentration of tailings is below the abundance in the crust (22.0 mg.kg<sup>-1</sup>). Terbium concentration varies from 0.3-14.3mg.kg<sup>-1</sup>. The concentration of the element in soil is above the average value in topsoil – 0.6mg.kg<sup>-1</sup>. The Sc concentration of tailings is below the abundance in the crust (1.2mg.kg<sup>-1</sup>). Yttrium concentration varies from 9.5-28.2mg.kg<sup>-1</sup>. The concentration of the element in soil is above the average value in topsoil – 21.0mg.kg<sup>-1</sup> only in SS1. The Sc concentration of tailings is below the abundance in the crust (33.0mg.kg<sup>-1</sup>). Ytterbium concentration varies from 1.0-2.3mg.kg<sup>-1</sup>. The concentration of the element in soil is above the average value in topsoil – 2.0mg.kg<sup>-1</sup> only in SS1. The Yb concentration of tailings is below the abundance in the crust (3.2mg.kg<sup>-1</sup>). It was found that light rare earth elements (LREEs) are in greater concentration in plant samples than heavy rare earth elements (HREEs). In fact, in post-mine sites, LREEs are typically 3 to 60 times more abundant than HREEs [14, 15].

The soil samples located near the beach of the tailings pond (SS1) contain higher concentrations of the studied elements than those located at the heel of the walls (SS3). According to the data, the soil layer contains higher concentrations of all elements than the tailings layer. Several factors may account for this. Rare elements exhibit an affinity for clay particles, while tailings have a gritty mechanical composition. In addition, the elements accumulate in organic layers on the surface [15]. The samples were taken at the end of October, after a long drought, which may have caused migration of the elements to the surface horizons through the Capillary Water Absorption. Moreover, the pH of the tailings is 4.2, which is highly acidic and is responsible for the mobility of the relevant metals in the tailings.

The contamination factor (CF) was calculated for all elements (Figure 1). On the basis of the obtained values, the investigated soils are characterised as lightly or moderately polluted. The highest value of CF was recorded in SS1. In all three sample points, the highest value of CF is with respect to Eu (CF<sub>ss1</sub> = 2.9, CF<sub>ss2</sub> = 2.3, and CF<sub>ss3</sub> = 2.1). The calculated contamination factor considers moderate contamination with respect to these elements (1 ≤ CF < 3 as moderate contamination). CF > 1 was found for all other elements (except for Dy (SS3), Ho (SS3), Lu (SS3), Y (SS2, SS3), and Yb (SS2, SS3)).

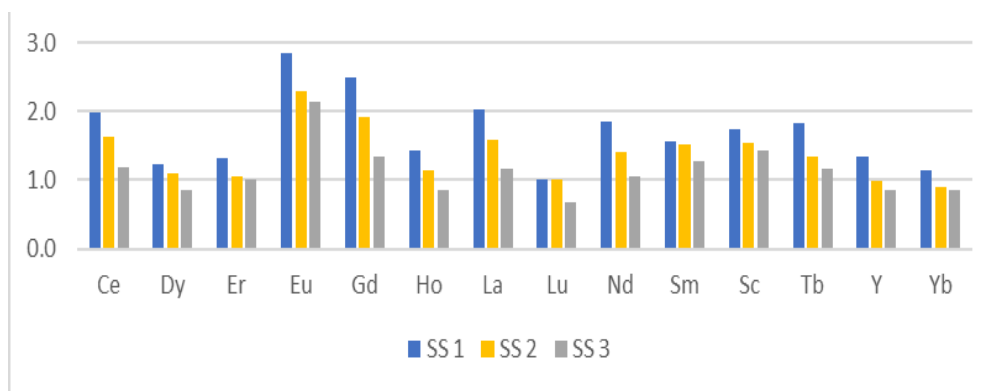


Fig. 1. Concentration factor

**REEs in plant biomass**

The contents of the studied rare earth elements in plant biomass (leaf) (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Sc, Sm, Tb, Y, Yb) are presented in Table 2.

REEs are neither essential to life nor toxic to the ecosystem. Rare earth elements are not essential for plants. However, plants are capable of absorbing REEs from the soil through their roots and through their leaves [15].

**Table 2.** The contents of the studied rare earth elements in plants biomass (leaf)

Element	<i>Euphorbia niciciana</i>	<i>Lolium perenne</i>	<i>Verbascum densiflorum</i>	<i>Cichorium intybus</i>	<i>Salix alba</i>	<i>Alnus glutinosa</i>	<i>Morus alba</i>	<i>Betula pendula</i>
				mg.kg <sup>-1</sup>				
Ce	5.81	13.07	5.16	1.81	0.62	0.38	0.32	0.21
Dy	0.24	0.70	0.30	0.12	0.03	0.02	0.02	0.03
Er	0.17	0.44	0.19	0.06	0.02	0.01	0.01	0.01
Eu	0.14	0.40	0.14	0.06	0.02	0.01	0.02	0.02
Gd	0.60	1.32	0.56	0.26	0.06	0.04	0.05	0.04
Ho	0.05	0.15	0.06	0.02	0.01	0.00	0.00	0.01
La	2.98	6.30	2.57	1.03	0.32	0.24	0.18	0.12
Lu	0.02	0.06	0.02	0.01	0.00	0.00	0.00	0.00
Nd	2.73	5.54	2.40	0.89	0.29	0.18	0.14	0.11
Sc	0.55	1.31	0.55	0.46	0.07	0.04	0.04	0.05
Sm	0.68	2.55	1.20	0.21	0.26	0.20	0.17	0.14
Tb	0.07	0.17	0.06	0.03	0.01	0.00	0.00	0.00
Y	1.27	3.77	1.48	0.51	0.19	0.12	0.10	0.13
Yb	0.12	0.42	0.15	0.06	0.02	0.01	0.01	0.01

According to Table 2, the concentration of cerium in plants varies between 0.21 and 13.07mg.kg<sup>-1</sup>. *Lolium perenne* contained the highest concentration of the element, followed by *Euphorbia niciciana* (5.81 mg.kg<sup>-1</sup>) and *Verbascum densiflorum* (5.16mg.kg<sup>-1</sup>). The concentration of Ce in the remaining plant species is below 1 mg.kg<sup>-1</sup>. The concentration of Ce in all plant parts is higher than the concentration of other REEs. This is consistent with the findings of many other studies. The determined concentration of the element in plants exceeds that found in the literature. According to it, plants in areas with mine tailings can accumulate high amounts of Ce 0.68 - 2.41mg.kg<sup>-1</sup> [16]. Dysponium concentration varies between 0.02 and 0.70mg.kg<sup>-1</sup>. The highest concentration of the element was again found in *Lolium perenne*, followed by *Verbascum densiflorum* (0.3mg.kg<sup>-1</sup>) and *Euphorbia niciciana* (0.24mg.kg<sup>-1</sup>). In the rest of the plant species, the concentration of Dy is below 0.05mg.kg<sup>-1</sup>. According to the literature data, this element is rarely detected in soils and plants by routine analytical methods, and, when detected, concentrations are generally low [17]. Erbium concentration varies between 0.0 and 0.44mg.kg<sup>-1</sup>. Again, the highest concentration of this element was found in *Lolium perenne*, followed by *Verbascum densiflorum* (0.14mg.kg<sup>-1</sup>) and *Euphorbia niciciana* (0.17mg.kg<sup>-1</sup>). In the remaining plant species, the concentration of Er is below 0.05 mg.kg<sup>-1</sup>. Europium concentration varies between 0.01-0.40mg.kg<sup>-1</sup>. The highest concentration of the element is again found in *Lolium perenne*, followed by *Euphorbia niciciana* and *Verbascum densiflorum*, with a concentration of 0.14mg.kg<sup>-1</sup>. In the literature, it has been found that the europium concentrations in plants vary from 0.016±0.015 mg/g. Gadolinium concentration varies between 0.04-1.32mg.kg<sup>-1</sup>. The highest concentration of the element was established in *Lolium perenne*, followed by *Euphorbia niciciana* (0.6mg.kg<sup>-1</sup>) and *Verbascum densiflorum* (0.56 mg.kg<sup>-1</sup>). In other plant species, the concentration of Gd is below 0.12mg.kg<sup>-1</sup>. It is known

that gadolinium is not retained by soil passage [18]. Holmium concentration varies between 0.0 and 0.15mg.kg<sup>-1</sup>. Again, the highest concentration of this element was found in *Lolium perenne*, followed by *Verbascum densiflorum* (0.06mg.kg<sup>-1</sup>) and *Euphorbia niciciana* (0.05mg.kg<sup>-1</sup>). In *Salix alba* and *Alnus glutinosa*, the element was not detected. Lanthanum concentration varies between 0.12-6.30mg.kg<sup>-1</sup>. The highest concentration of the element was found in *Lolium perenne*, followed by *Euphorbia niciciana* (2.98mg.kg<sup>-1</sup>) and *Verbascum densiflorum* (2.57mg.kg<sup>-1</sup>). In the remaining plant species, the concentration of La is below 0.4mg.kg<sup>-1</sup>. Wiche and Heilmeyer found the mean concentrations of La as representative for the REEs ranged from 24 to 146ng.g<sup>-1</sup> in grasses (*Hordeum vulgare*, *Zea mays*, *Avena sativa*, *P. miliaceum*, and *Phalaris arundinacea*) and 20–250ng.g<sup>-1</sup> in herbs (*Lupinus albus*, *Lupinus angustifolius*, *Fagopyrum esculentum*, and *Brassica napus*) when grown in soil from a road construction site or mining affected area containing 25–26µg.g<sup>-1</sup> total La. In other studies, it was found that in areas with mine tailings, plants can accumulate high amounts of La 0.45-0.57mg.kg<sup>-1</sup> [19]. In the present case, the three species accumulate up to 10 times more. Lutetium concentration varies between 0.0 and 0.06mg.kg<sup>-1</sup>. The highest concentration of the element is again found in *Lolium perenne*, followed by *Euphorbia niciciana* and *Verbascum densiflorum*, with a concentration of 0.02mg.kg<sup>-1</sup>. In other plant species, the element has not been identified. Neodymium concentration varies from 0.11-5.54mg.kg<sup>-1</sup>. The highest concentration of the element was found in *Lolium perenne*, followed by *Euphorbia niciciana* (2.73mg.kg<sup>-1</sup>) and *Verbascum densiflorum* (2.40mg.kg<sup>-1</sup>). In the remaining plant species, the Nd concentration is below 0.4 mg.kg<sup>-1</sup>. Nd concentrations in the plants ranged between 40 and 3 700µg/kg for the roots and 0.3 to 15µg/kg for the trunk [19]. Samarium concentration varies between 0.04-1.31mg.kg<sup>-1</sup>. Again, the highest concentration of this element is found in *Lolium perenne*, followed by *Euphorbia niciciana* and *Verbascum densiflorum*, with a concentration of 0.55mg.kg<sup>-1</sup>. In the rest of the plant species, the concentration of Sm is below 0.1mg.kg<sup>-1</sup>. A concentration of the element was found in the range of 0.16-0.02mg.kg<sup>-1</sup> (for alfalfa) during the research studies [20]. In the present case, the detected concentration was up to 9 times higher [21]. Scandium concentration varies between 0.14-2.55mg.kg<sup>-1</sup>. Again, the highest concentration of this element was found in *Lolium perenne*, followed by *Verbascum densiflorum* (1.2mg.kg<sup>-1</sup>) and *Euphorbia niciciana* (0.68mg.kg<sup>-1</sup>). In the rest of the plant species, the concentration of Sc is below 0.4mg.kg<sup>-1</sup>. The uptake and bioaccumulation of Sc are not well understood. There is only one conclusion that can be drawn from this study, namely that high concentrations of Sc in plants are rather rare. Sc concentrations in plants are much lower than those in soils under ordinary conditions, indicating that no bioaccumulation occurs [22]. Terbium concentration varies between 0.0-0.17mg.kg<sup>-1</sup>. The highest concentration of the element was found in *Lolium perenne*, followed by *Euphorbia niciciana* (0.07mg.kg<sup>-1</sup>) and *Verbascum densiflorum* (0.06mg.kg<sup>-1</sup>). In the species *Salix alba* and *Morus alba*, the element was not detected. Yttrium concentration varies between 0.10-3.77mg.kg<sup>-1</sup>. Again, the highest concentration of this element was found in *Lolium perenne*, followed by *Verbascum densiflorum* (1.48mg.kg<sup>-1</sup>) and *Euphorbia niciciana* (1.27mg.kg<sup>-1</sup>). In the remaining plant species, the concentration of Y is below 0.4 mg.kg<sup>-1</sup>. Ytterbium concentration varies between 0.01-0.42mg.kg<sup>-1</sup>. Again, the highest concentration of this element was found in *Lolium perenne*, followed by *Verbascum densiflorum* (0.15mg.kg<sup>-1</sup>) and *Euphorbia niciciana* (0.12mg.kg<sup>-1</sup>). In the remaining plant species, the concentration of Yb is below 0.04mg.kg<sup>-1</sup>.

Except for hyperaccumulating plants, the content of REEs in plants is generally very low [23]. The obtained results show that none of the investigated plant species can be considered a hyperaccumulator of REEs, since the obtained REE content in the plant's upper parts was less

than 1000mg.kg<sup>-1</sup>. The highest content of all the investigated elements is found in *Lolium perenne*, followed by *Verbascum densiflorum* and *Euphorbia niciciana*. *L. perenne* is widely used for phytotoxicity tests due to the fact that it is sensitive to many chemicals. Also, *Lolium perenne* is considered one of 73 species tolerant of various environmental stresses [24, 25], and *Verbascum densiflorum* is known as a pioneer species for contaminated and recultivated mining sites due to its high tolerance to heavy metals, possibly rare ones as well [26, 27]. For the genus *Euphorbia*, it is known that some species are also known as hyper-accumulators of heavy metals and are appropriate candidates for phytoremediation. There is no data specifically for *Euphorbia niciciana*.

A bioaccumulation coefficient was calculated for all plant species (Fig. 2).

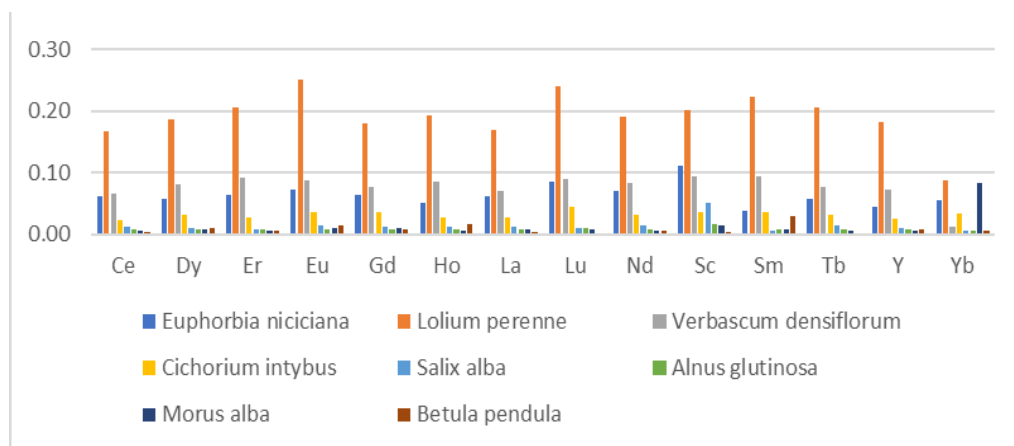


Fig. 2. Bioaccumulation factor

Based on the data obtained, none of the investigated plant species exhibits a bioaccumulation coefficient below 1.0. It was found that *Lolium perenne* had the highest bioaccumulation coefficient in relation to all the elements examined. The bioaccumulation of the elements follows the following order: Eu > Lu, Yb > Sm > Eu > Sc, Tb > Ho, La, Dy > Y, Gd > Ce. The highest value found for BCF is 0.24 for Eu, 0.24 for Lu and Yb, and 0.22 for Sm. In other studies, the same bioaccumulation coefficient was found for Eu (25% of the total amount of bound europium was detected inside the leaves). Yb and Y were 3 to 4 times more extractable than La, Ce, Sm, and Gd; it's also known that LREEs were also slightly more bioaccumulated. This is only confirmed for Yb.

A bioaccumulation coefficient of 0.1 was obtained for the remaining plant species. In the present study, low bioaccumulation factors were observed. This indicates that only very small proportions of these elements in soils were present in plant-available fractions and transferred to plants, likely due to the high soil pH, under which REE mobility and bioavailability are low.

In other literature submissions, the BCF for Ce was the lowest. The results obtained confirm this statement. Such results may contribute to the differences in bioaccumulation factors among REEs. Under most geochemical conditions, REEs form 3<sup>+</sup> cations; however, Ce is redox-sensitive and occurs in soils in two oxidation states, Ce<sup>3+</sup> and Ce<sup>4+</sup>. The mobility and metastability of Ce<sup>4+</sup> are considerably reduced compared to Ce<sup>3+</sup>. As compared to other REEs, it is incorporated more readily into Mn and Fe oxides and hydroxides. A strong negative Ce-

anomaly has been observed in some vascular plants because of reduced uptake of  $Ce^{4+}$  compared to  $Ce^{3+}$  [28].

A trend for BFC values in the following order:  $Y > Sc > La > Ce$ , or  $Sc > Y > La > Ce$ , was inferred. In the present case, the order for *L. perenne* is as follows:  $Sc > La > Y > Ce$ .

A low bioaccumulation factor for REEs may also indicate that plants have a barrier to REE absorption and translocation [29].

## Conclusions

This study reveals that the rare earth metal content in recultivated terrain exceeds the average level found in soils. It has been reported that Eu has the highest concentration factor ( $CF_{ss1} = 2.9$ ,  $CF_{ss2} = 2.3$ , and  $CF_{ss3} = 2.1$ ). For all other elements (with the exception of Dy (SS3), Ho (SS3), Lu (SS3), Y (SS2, SS3), and Yb (SS2, SS3),  $CF > 1$  was found.

The order of bioaccumulation of the elements is  $Eu > Lu$ ,  $Yb > Sm > Eu > Sc$ ,  $Tb > Ho$ ,  $La$ ,  $Dy > Y$ , and  $Gd > Ce$ . There were no hyperaccumulators detected for any of the elements investigated. The highest concentrations of the studied elements were found in *Lolium perenne*, *Verbascum densiflorum*, and *Euphorbia nicifiana*.

Based on these results, the site may be a suitable site for future phytomining research.

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