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ELEMENTAL ANALYSIS OF CONTAMINATED BIOMASS ASHES FOR PHYTOMINING OF RARE EARTH ELEMENTS

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ABSTRACT

Phytomining of rare earth elements (REEs) provides a potential possibility for metal recovery at brownfields where conventional mining technique is not reasonable or profitable. The holistic concept of phytomining is instituted from three scientific sectors. Phytoextraction is the first stage referred to accumulation of REEs in plants. This is followed by the enrichment process aiming to elevate metal concentration into solid remains. Eventually, extraction technology is applied to reclaim these valuable metals from the bio-ores. The main goal of this study is to identify a possible location for REEs phytomining, which lays the groundwork for further investigations. To do that, different woody biomass from disparate contaminated spots was harvested and examined. A brownfield land located in Gyöngyösoroszi, Hungary has been selected based on the elemental analysis of ash samples obtained from the incineration of the collected plants at 500 °C. The outcomes also preliminarily indicate the viability of phytomining in recovering REEs.

Keywords: brownfields, phytoextraction, rare earth metals, recovery, chemical analysis

1. INTRODUCTION

Rare earth elements (REEs) include scandium (Sc), yttrium (Y), and 15 "lanthanides" elements from lanthanum (La) to lutetium (Lu) [1]. REEs are playing an important role in green modern technologies such as hybrid cars, electric cars, wind turbines, batteries, etc [2]. These metals are also commonly used as fertilizers in agriculture to advance the quality and production of crops [3], [4]. The demand for REEs has increased remarkably causing reserve depletion, while the recycling rate reportedly is only 1% [2]. Hence, the recovery of REEs from secondary resources is a crucial issue, that has attracted a great deal of global attention in recent decades.

Phytomining is a potential manner for recycling REEs from contaminated soils where traditional mining technology is not competitive. The entire procedure of phytomining encompasses three scientific sectors; these are phytoextraction, enrichment, and extraction. At the first stage, REEs from polluted lands are accumulated in plants via phytoextraction. Two types of plants that could be efficiently used for this process are hyperaccumulators and fast-growing species [5]. In the following phase, the contaminated biomass is reduced to a manageable volume, and more importantly, these valuable metals are enriched into solid remains called bio-ores. A number of methods can be applied to achieve the enrichment purpose, which is composting, compaction, and thermal conversion (ashing, pyrolysis, gasification, combustion). Of these options, combustion is considered the most feasible and ecologically friendly manner for heightening REEs [6], [7]. Eventually, conventional or innovative extraction technologies could be utilized to extract REEs from bio-ores [8]. That is the last step to complete the phytomining route of recovering REEs from brownfield lands.

The complete approach of phytomining has been intensively investigated and widely applied to recover Nickel from polluted soils [9]–[13]. More than 500 plant species have been verified to hyper-accumulate this element [14]. The agronomic processes alongside extraction techniques have been extensively developed to produce Ni-based products such as oxide, metal, and salts [15], [16]. In another study, the whole phytomining pathway for reclaiming noble metals has been disclosed [17]. While this concept is somewhat novel in terms of REEs. The main goal of this study is to determine the possible location for the phytomining of REEs. It is

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paramount as these elements are mostly dispersed in low concentrations throughout the earth's crust [18]. Identifying the viable area helps to lay the groundwork for the further steps of REEs phytomining.

2. MATERIALS AND METHODS

The resource of the contaminated biomass utilized in this research is a polluted region situated in Gyöngyösoroszi, Hungary (Mátra Mountains, Northern Hungary). In fact, it is an abandoned mining area where lead and zinc industrialized mining started in 1926 and closed in 1986 after 40 years of operation. The common plant species living there include poplar, oak, birch, pine, walnut, wattle, and bushes. Four sampling sites namely A, B, C, and D have been assigned in the abandoned mining zone, their exact locations are presented in Figure 1 and Table 1. From these places, different woody biomass comprising root and log (trunk) were collected as chemical elements are not distributed evenly in plant parts.

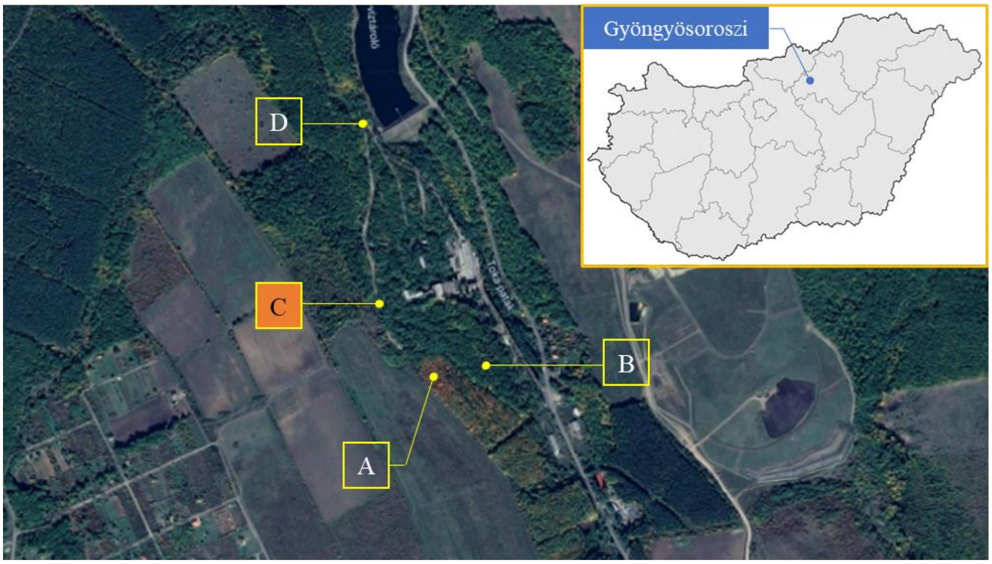

Figure 1. Sampling sites in Gyöngyösoroszi, Hungary

Table 1. The exact coordinates of the sampling sites

Sampling site	Latitude	Longitude
A	47.8420957	19.8772271
B	47.8423633	19.8785983
C	47.8434655	19.8758115
D	47.8469843	19.8752731

The harvested biomass was cleaned and rinsed in the case of root samples. Then, the biomass was left in the laboratory under natural conditions for several weeks for air drying. This was followed by drying in the oven at 105 °C for 24 hours. Afterward, the collected samples were incinerated by two-stages ashing processes. In the first step, the dried biomass was heated at 250 °C, for 2 hours with a heating rate of 50 °C/h. In the second stage, the process was carried out under the conditions as follows: heating rate 50 °C/h up to 500 °C, 4 hours waiting at 500 °C. The operation was conducted two times to secure carbon-free ash samples. The ashing temperature applied for the polluted biomass is based on previous publications [19], [20].

The chemical composition of ash samples was determined by ICP (Inductively Coupled Plasma) spectrometry, using Perkin Elmer Avio 200 inductively coupled plasma-optical emission spectrometer (ICP-OES). For the calibration of the measurement, an ICP-OES inner standard solution (Lutecium) was used. The samples were prepared based on the Hungarian standard MSZ EN 13346:2000. The analytical scale was used for taking 5 g samples for analysis. The preparation was carried out by microwave digestion with a Berghof Speedwave4 laboratory equipment, using nitric acid (2 ml, 67% concentrated) and hydrochloric acid (6 ml, 36% concentrated) solvents. The digestion and dissolution time were 30 minutes at 180 °C. The solution was filled up to 50 ml with 5% concentrated nitric acid after the filtration process using MN616 filters. The chemical measurement analyzes the concentrations of almost REEs (including Ce, Dy, Er, Eu, Gd, Ho, La, Nd, Pr, Sc, Sm, Tb, Tm, Y, Yb) in the ash samples.

3. RESULTS AND DISCUSSION

The ICP spectrometry analysis results regarding REEs concentrations in the ash samples of log and root biomass gathered from different polluted sites are shown in two tables corresponding to two metal groups. The first metal group presented in Table 2 includes Er (Erbium), Ho (Holmium), Pr (Praseodymium), Tb (Terbium), and Tm (Thulium). These elements are below the detection limit (BDL) in all the ash samples, and they are not used for further evaluations.

Table 2. Metal concentrations below the detection limit in ash samples

Element	Concentration (mg/kg)							
	Log ash				Root ash			
	A	B	C	D	A	B	C	D
Er	*<1**	*<1**	*<1**	*<1**	*<2**	*<1**	*<2**	*<1**
Ho	*<1**	*<2.5**	*<2.5**	*<2.5**	*<2.5**	*<2.5**	*<2.5**	*<1**
Pr	*<5**	*<5**	*<5**	*<5**	*<5**	*<5**	*<5**	*<5**
Tb	*<5**	*<2**	*<2**	*<2**	*<2**	*<2**	*<2**	*<5**
Tm	*<1**	*<1**	*<1**	*<1**	*<1**	*<1**	*<1**	*<1**

- A, B, C, D: sampling points
- * The concentration of the metal is BDL (below the detection limit), which is the limit that the concentration can be differentiated from the background noise.

The second metal group consists of Ce (Cerium), Dy (Dysprosium), Eu (Europium), Gd (Gadolinium), La (Lanthanum), Nd (Neodymium), Sc (Scandium), Sm (Samarium), Y (Yttrium) and Yb (Ytterbium); which are observed in at least one sample. They are given in Table 3 and are used for further investigations. The concentration magnitudes were colorized in the increasing order of green-yellow-red (Table 3). Besides that, the measurement results were also visualized into graphs shown in Figure 2.

Table 3. The concentration of detectable REEs in ash samples of biomass gathered from different contaminated sites

Element	Concentration (mg/kg)							
	Log ash				Root ash			
	A	B	C	D	A	B	C	D
Ce	*<1**	*<2**	3.12	3.72	41.69	7.14	29.49	17.81
Dy	*<2**	*<2**	*<2**	*<2**	3.20	*<2**	*<2**	*<2**

Element	Concentration (mg/kg)							
	Log ash				Root ash			
	A	B	C	D	A	B	C	D
Eu	<0.5*	<0.5*	<0.5*	<0.5*	0.67	<0.5*	0.78	<0.5*
Gd	<1*	2.55	2.52	1.68	9.93	3.38	6.60	<2*
La	1.43	0.75	2.20	2.43	23.68	4.52	13.45	10.90
Nd	<1*	<1*	<1*	<1*	18.13	<5*	14.70	6.30
Sc	<0.5*	<0.5*	<0.5*	<0.5*	7.23	1.86	7.75	3.82
Sm	<1*	<1*	<1*	<1*	5.56	<2*	4.73	2.53
Y	0.64	<0.5*	0.77	1.30	17.79	5.61	10.47	10.13
Yb	<2.5*	<0.5*	<0.5*	<0.5*	1.81	<0.5*	1.02	<2.5*

- A, B, C, D: sampling points
- * The concentration of the metal is BDL (below the detection limit), which is the limit that the concentration can be differentiated from the background noise.

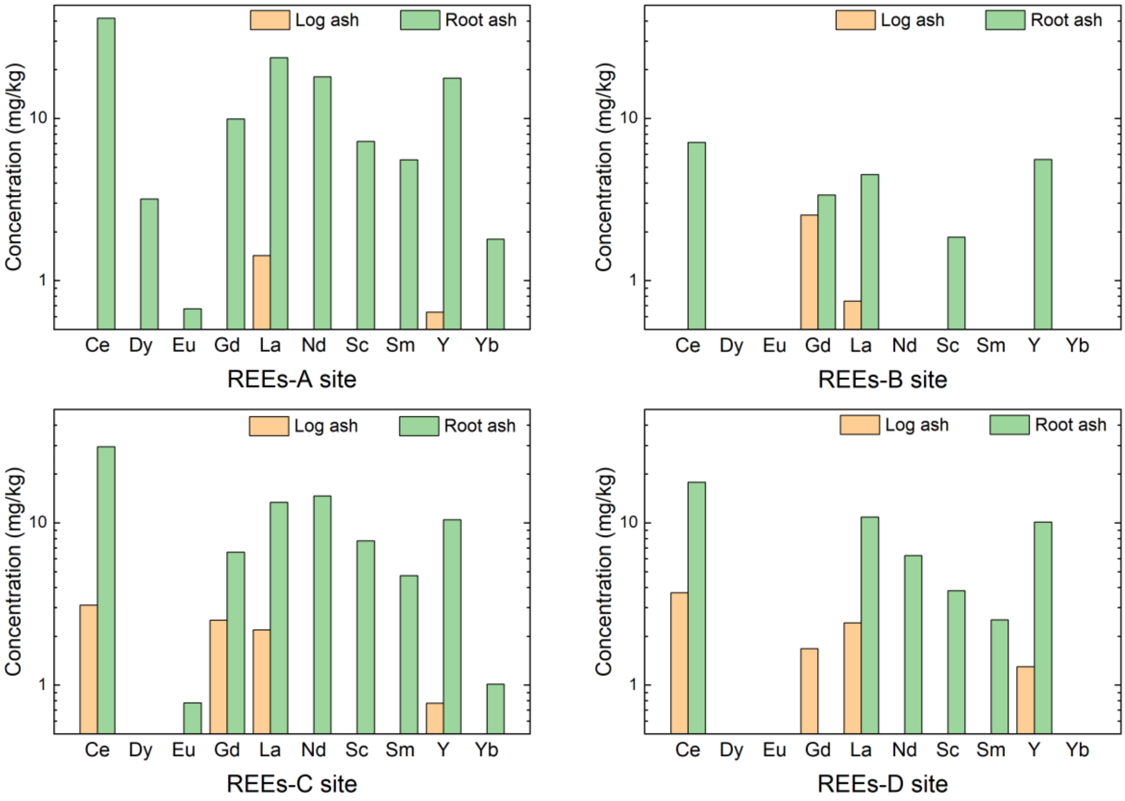

Figure 2. The concentration of REEs in the log and root ash samples of biomass gathered from different contaminated sites

In terms of log ash and root ash together, REEs were most identified in the samples collected from the C site (Figure 2). To be specific, four elements comprising Ce, Gd, La, and Y were found in both log and root ash samples, and five more REEs (Eu, Nd, Sc, Sm, Yb) were detected in root ash of biomass coming from this area. The concentration of REEs in the solid remains obtained from polluted site C is quite high compared to that in other sampling points. Because of the mentioned reasons, site C has been selected as the attainable location for further investigations of REEs phytomining.

REEs were considerably detectable, ten of those elements were determined in the ash of biomass gathered from the brownfields. Their concentrations are in a wide range from less than one to dozens of ppm. The elements such as Europium and Ytterbium were barely found, while Cerium, Lanthanum, and Samarium showed the highest concentrations of 41.69, 23.68, and 18.13 mg/kg respectively in the ash of biomass harvested from location A. In terms of total rare earth minerals, the levels are as high as 130 and 89 mg/kg observed in root ashes of the A and C sites. These numbers are relatively high, so extraction of REEs from ashes coming from contaminated biomass has great potential.

The graphs in Figure 2 also present the distribution of REEs. It indicates that the concentration of REEs in the root ash is higher than in the log ash. The results are in good agreement with other studies [21]–[23]. That can be explained by the distribution of metals in the below-ground part (root). It is usually higher than in log [24], [25] but other above-ground parts (foliage, leaves, etc.) could also accumulate higher concentrations of them [22], [26].

4. CONCLUSIONS

In the spirit of specifying an attainable location for REEs phytomining, different types of woody biomass encompassing root and log were collected from four metal-polluted sites located in Gyöngyösoroszi, Hungary. The harvested plants were incinerated at 500 °C to generate ashes for ICP analysis. According to the elemental analytical outcomes, the contaminated spot C has been chosen for further research of REEs phytomining due to the following reasons. In terms of log ash and root ash together, REEs were most detected in the samples gathered from there. The concentrations of the detectable metals in the solid residuals from site C are relatively high compared to other sampling points. The chemical measurements also indicate that the concentration of REEs in the root ash is higher than that in the log ash, which is an essential input for further investigations. It is worth noting that the concentration of REEs is significant in bio-ores obtained from contaminated biomass, and the solid remains are promising metal resources. In the following work, the plants coming from selected location C would be combusted. Solid residues such as bottom ash, fly ash, and deposited ash from several positions in the combustion and flue gas system will be captured and analyzed. Further directions would be defined on the basis of the chemical analysis results.

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