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DISTRIBUTION OF METALS WITHIN DIFFERENT PLANT PARTS OF BIOMASS GATHERED FROM A BROWNFIELD LAND LOCATED IN GYÖNGYÖSOROSZI, HUNGARY

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Abstract: The development of modern technologies requests increasing demand for rare earth elements (REEs) and noble metals (NMs). That has spurred mining activities and has released metals into the environment as a consequence. Phytoextraction uses plants to accumulate metals into their shoots enabling metal removal from brownfields (phytoremediation) or recovery of valuable metals (phytomining). Nevertheless, the occurrence and distribution of NMs, REEs in biomass coming from contaminated lands have not been intensively investigated yet.

In this study, different types of woody biomass including root, trunk, branches, and leaf were collected from a metal-polluted location in Gyöngyösoroszi, Hungary. Afterward, the harvested plants were combusted at 500 °C to generate ashes for ICP (Inductively Coupled Plasma) analysis. Elemental analytical results show that a couple of NMs such as Ag, Au, Pt were found and distributed differently in various biomass ash samples. In specific, the highest Ag concentration is around 5.4 mg/kg achieved in the root ash. Meanwhile, the greatest number of Au and Pt is about 1.8 mg/kg obtained in the trunk and leaf ash respectively. Besides, several REEs with substantial quantities were identified in the contaminated biomass ashes. The significant results observed in the root ash are approximately 47.8 mg/kg Ce and 30.5 mg/kg Nd. The concentration of REEs in root ash is higher than in the above-ground biomass ash with the decreasing order of root ash, leaf ash, trunk, and branches ash. It can be explained by the distribution of REEs in root or leaf is usually greater than other plant parts. These valuable findings indicate that phytomining is a promising approach for recycling NMs, REEs from soils via plants. Moreover, solid residues obtained from polluted biomass are potential metal resources.

Keywords: Biomass, noble metals, rare earth elements, phytoextraction, phytomining

INTRODUCTION

Nowadays, in the context of industrialization and urbanization, the concentration of metals in soils has been increasing significantly resulting in environmental problems and brownfield lands [1]. According to the reported data, more than one-third of the

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global land is polluted [2]. The real number even could be greater than what has been unveiled so far. On the other hand, the growth of metals in soil surface simultaneously provides the opportunity for extracting metals from contaminated areas.

Phytoextraction using plants to accumulate metals from soils for removing metals from brownfields refers to phytoremediation [3]–[5]. Additionally, this technique offers the possibility for exploiting valuable metals from mill tailings, overburdens, low-grade ores, or mineralized soil that is not economic by traditional mining methods referred to as phytomining [6]–[8]. Phytoextraction has been proven as an effective, environmentally friendly, safe, and low-cost soil remediation technology [9]–[11], as well as the potential for recovering metals from secondary resources [12]–[14]. Nonetheless, most studies focus on heavy metals such as Ni, Zn, Cd, etc [15]–[19], meanwhile, less attention has been paid in the case of valuable metals including NMs and REEs [20]–[22]. The presence of NMs and REEs in plants was reported in some studies [6], [23]. Concentrations of these valuable metals have been barely investigated showing disparities between different plant parts. Several investigations have verified that the concentration of NMs in the below-ground part (root) is usually higher than in the above-ground parts (stems, leaves) [21], [24]. On the other hand, other studies have verified the declining REEs concentrations in the order of leaf > root > stem [25], [26].

This research investigates the occurrence and distribution of metals comprising NMs and REEs in ligneous plants gathered from a polluted site. In the whole picture of phytomining, plants used for phytoextraction are combusted, following that NMs, REEs are reclaimed from the solid remains. Before the combustion of contaminated biomass is conducted, analyzing valuable metals in ash samples obtained by ashing polluted biomass is essential. This analysis assists to evaluate the feasibility of the phytomining technique and determine the possibility of the further process of combustion.

1. MATERIAL AND METHOD

The source of the biomass utilized in this study is brownfield land in Gyöngyösoroszi, Hungary. In fact, it is an abandoned mining area where industrial lead and zinc production was operating until 1986. The common ligneous plant species living there are oak, pine, wattle, walnut, birch, poplar, and bushes, etc. Different plant parts comprehending root, trunk, branches, and leaf have been collected. The collected woody biomass was cleaned and washed in the case of root samples. They were left at the laboratory under natural conditions in a few weeks for air drying. Afterward, the collected plants have been dried in the oven at 105 °C for 24 hours. This was followed by two-stages ashing processes in the furnace. In the first stage, the dried samples were heated for 2 hours at 250 °C with a heating rate of 50 °C/h. In the second step, the process was continued under the following conditions: heating rate 50 °C/h up to 500 °C, 4 hours waiting at 500 °C. The operation was run twice to ensure carbon-free ash samples. The ashing temperature of contaminated biomass is based on some published studies [27], [28].

The chemical analysis of ash samples was performed by an individual company in Hungary, 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 Speedwave 4 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 concentration of 38 elements including REEs (Ce, Dy, Er, Eu, Gd, Ho, La, Nd, Pr, Sc, Sm, Tb, Tm, Y, Yb), NMs (Ag, Au, Ir, Os, Pd, Pt, Ru, Rh), and others (Cd, Co, Cr, Fe, Mg, Mn, Mo, Na, Ni, Pb, Th, Ti, U, V, Zn) was assigned to identify due to their essentials, high economic value, or toxicity.

2. RESULT AND DISCUSSION

The ICP spectrometry analysis results regarding metal content (up to 38 elements) in ash samples of different types of biomass namely root, trunk, branches, and leaf collected from the contaminated location are given in two tables corresponding to two metal groups. The first metal group shown in Table 1 summarizes elements that are below the detection limit (BDL) in each sample. It can be seen that several NMs (Ir, Os, Pd, Rh, Ru) belong to this group along with a couple of REEs (Ho, Pr, Tb, Tm) and other metals (Th, U). These metals were not used for further evaluations.

Table 1

Metals below the detection limit in ash samples of gathered polluted biomass

Element		Concentration (mg/kg)			
Symbol	**Name**	**Root ash**	**Trunk ash**	**Branches ash**	**Leaf ash**
Ir	Iridium	*<2**	*<1**	*<1**	*<1**
Os	Osmium	*<1.5**	*<1.5**	*<1.5**	*<1.5**
Pd	Palladium	*<2**	*<1**	*<1**	*<1**
Rh	Rhodium	*<1**	*<1**	*<1**	*<1**
Ru	Ruthenium	*<2**	*<2**	*<2**	*<2**
Ho	Holmium	*<1**	*<0.5**	*<0.5**	*<0.5**
Pr	Praseodymium	*<5**	*<3.5**	*<3.5**	*<3.5**
Tb	Terbium	*<1**	*<1**	*<1**	*<1**
Tm	Thulium	*<0.5**	*<0.5**	*<0.5**	*<0.5**
Th	Thorium	*<6**	*<3**	*<3**	*<3**
U	Uranium	*<10**	*<10**	*<10**	*<10**

* 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 consisting of some NMs (Ag, Au, Pt), REEs (Ce, Dy, Er, Eu, Gd, La, Nd, Sc, Sm, Y, Yb) and others (Cd, Co, Cr, Fe, Mg, Mn, Mo, Na, Ni, Pb, Ti, V, Zn) which are detectable in at least one sample. These elements depicted in *Table 2* were used for further investigations. In each metal group, the concentration magnitudes were colored in the increasing order of green-yellow-red.

A couple of NMs such as Ag, Au, Pt were detected and distributed differently in various biomass ash samples *(Figure 1)*. The highest content was 5.369 mg/kg of Ag achieved in the root ash. The other woody ashes (trunk ash, branches ash) performed the same level of 1 mg/kg Ag. While the maximum concentration of Au obtained in trunk ash was 1.880 mg/kg. Au grade of the others ranges from 0.774 to 1.322 (mg/kg) in an ascending sequence: branches ash < leaf ash < root ash. The measurement also shows a considerable amount of Pt was obtained in the collected biomass ashes; its concentrations were in decreasing order of leaf ash (1.848 mg/kg), trunk ash (1.587 mg/kg), and branches (1.002 mg/kg).

Table 2

The concentration of detectable metals in ash samples of gathered polluted biomass

Element		**Concentration (mg/kg)**			
Symbol	**Name**	**Root ash**	**Trunk ash**	**Branches ash**	**Leaf ash**
Noble metals					
Ag	Silver	5.369	1.000	1.000	*<0.5**
Au	Gold	1.322	1.880	0.774	1.215
Pt	Platinum	*<3**	1.587	1.002	1.848
Rare earth elements					
Ce	Cerium	47.755	3.136	2.991	4.557
Dy	Dysprosium	3.942	*<1**	*<1**	*<1**
Er	Erbium	1.897	*<1**	*<1**	*<1**
Eu	Europium	1.660	*<0.25**	*<0.25**	*<0.25**
Gd	Gadolinium	6.467	*<0.5**	*<0.5**	*<1**
La	Lanthanum	20.938	2.558	2.410	3.732
Nd	Neodymium	30.487	1.384	1.538	2.900
Sc	Scandium	8.168	*<0.2**	*<0.2**	*<0.2**
Sm	Samarium	7.485	*<0.5**	*<0.5**	0.549
Y	Yttrium	19.599	1.000	1.344	3.479
Yb	Ytterbium	1.654	*<0.2**	*<0.2**	*<0.2**

Element		Concentration (mg/kg)			
Symbol	**Name**	**Root ash**	**Trunk ash**	**Branches ash**	**Leaf ash**
Other elements					
Cd	Cadmium	170.898	182.909	79.557	82.590
Co	Cobalt	7.342	2.488	1.811	6.677
Cr	Chromium	14.444	3.082	1.606	4.652
Fe	Iron	29,325.561	690.910	605.501	1,254.860
Mg	Magnesium	18,839.407	22,781.691	21,641.779	24,486.568
Mn	Manganese	1,241.806	955.740	1,028.223	1,249.890
Mo	Molyb-denum	1.773	1.360	2.504	0.576
Na	Sodium	1,092.936	3,134.986	965.733	1,030.830
Ni	Nickel	9.752	2.553	4.210	6.823
Pb	Lead	2,289.551	35.294	20.042	12.430
Ti	Titanium	259.383	16.010	17.426	26.682
V	Vanadium	31.452	*<1**	*<1**	*<1**
Zn	Zinc	27,237.674	6,177.369	6,765.875	8,869.407

* 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.

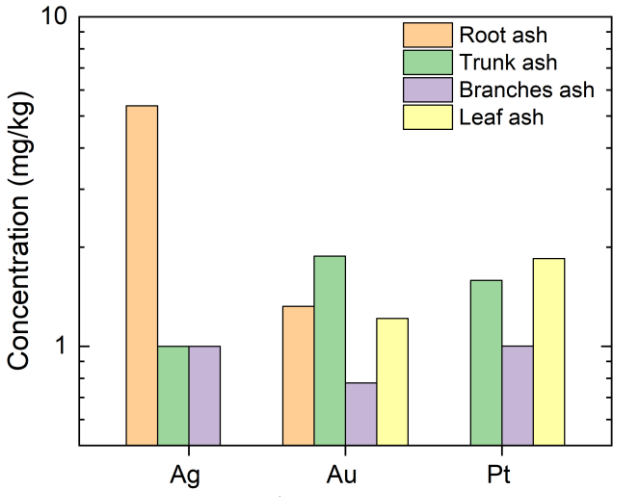

Figure 1

The concentration of NMs in contaminated biomass ash samples

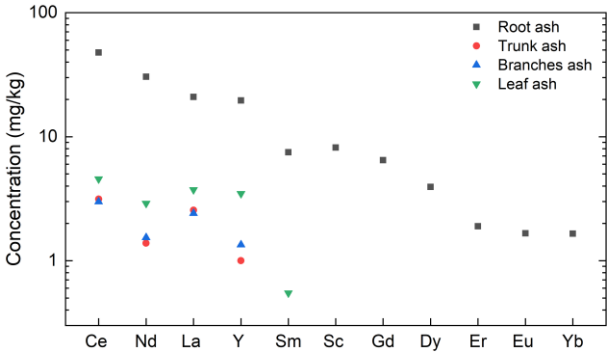

Figure 2

The concentration of REEs in contaminated biomass ash samples

Several REEs with substantial quantities were identified in the contaminated biomass ashes. A few elements comprehending Ce, Nd, La, and Y which presented in all the ash samples. The other metals except Sm were only detectable in the root ash as seen in *Figure 2*. Furthermore, the figure indicates that the concentration of REEs in root ash is higher than in the above-ground biomass ash with the following order: root ash > leaf ash > trunk, branches ash (trunk ash and branches ash performed the same trend). That can be explained by the distribution of REEs in root or leaf is usually higher than other plant parts. The significant results observed in the root ash were 47.755 mg/kg Ce, 30.487 mg/kg Nd, 20.938 mg/kg La, 19.599 mg/kg Y. Meanwhile, REEs were modestly distributed from 0.549 to 4.557 mg/kg in the other samples.

Other elements including heavy metals were also analyzed in this study. Their concentrations varied in a wide range of 0.576 ÷ 29,325.561 mg/kg. The notable findings were 29,325.561 mg/kg Fe and 27,237.674 mg/kg Zn in root ash; 24,486.568 and 22,781.691 mg/kg of Mg in leaf ash and trunk ash respectively. On the basis of Figure 3, to some extent, the contents of these elements in the aerial tissue ash comprising trunk ash, branches ash, leaf ash presented the similarity. It was likely smaller than the concentrations in the root ash (as seen, the dark point mainly above the others).

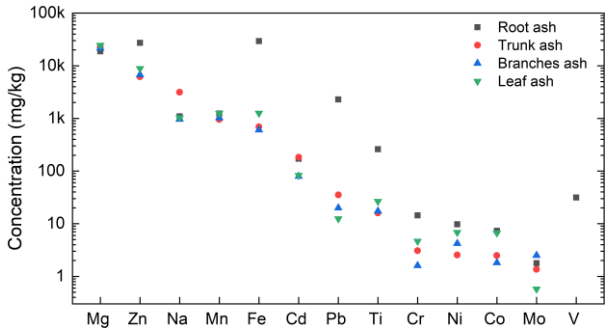

Figure 3

The concentration of other elements in contaminated biomass ash samples

CONCLUSIONS

Chemical analysis results revealed that NMs were detectable in the contaminated biomass ash incinerated at 500 °C. In particular, 5.369 mg/kg of Ag and 1.322 mg/kg of Au were found in the root ash. Meanwhile, in the ash of the trunk Ag, Au and Pt were observed at levels of 1; 1.88; and 1.587 mg/kg respectively. A considerable amount of REEs was identified in the ash samples. The concentration of these elements in the root ash is greater than in the ash of above-ground plant parts in the decreasing order: root ash > leaf ash > trunk, branches ash. This is in complete agreement with the previous studies [29], [30]. Large quantities of other metals including heavy metals were also identified in the polluted biomass ash samples. To some extent, their concentrations performed the similarity in aerial tissue ashes and were likely smaller than the metal contents in the root ash.

The detections of NMs and REEs in the contaminated biomass ashes lay the groundwork and demonstrate the viability of phytomining in recovering valuable metals. In the following stage, the polluted plants will be combusted. Solid remains such as bottom ash, fly ash, deposited ash from different positions in the combustion and flue gas system would be collected and analyzed. Based on the elemental analysis outcomes, further directions would be defined.

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