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Field study on Re and heavy metal phytoextraction and phytomining potentials by native plant species growing at Sarcheshmeh copper mine tailings, SE Iran

S. Tabasi, H. Hassani* and A.R. Azadmehr

Mining and Metallurgical Engineering Department, Amirkabir University of Technology, (Tehran Polytechnic), Tehran, Iran

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**Corresponding author: hhassani@aut.ac.ir (H. Hassani).*

Abstract

In the present work, we aimed to focus on the identification and characterization of the heavy metal-tolerant plant species growing spontaneously at the tailings site of the Sarcheshmeh copper mine, south of Iran. Our aim was to find the plant species that were potentially useful for phytoextraction purposes. The concentrations of As, Cu, Mo, Ni, Zn, and Re were analyzed in soil as well as in the shoots and roots of plant species separately by an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP–OES). The mean concentrations of As, Cu, Mo, Ni, Zn, and Re in soil were found to be 18.44±13.41, 1280±500.95, 25.06±13.33, 32.9±14.39, 251.82±95.82, and 1.7±0.78 mg kg^{-1}, respectively. The translocation factor (TF) and the bioaccumulation factor (BCF) were defined and used to assess the amount of the elements accumulated in the shoots and roots of each plant species and to evaluate their potential for phytoextraction purposes. Based upon the results obtained and using the most common criteria, *T. ramosissima, C. dactylon*, *A. leucoclada*, and *Z. fabago* could strongly tolerate and extremely accumulate multiple metal(loid)s. Also *Salsola kali*, *C. dactylon*, *A. leucoclada*, and *Z. fabago* could be classified as hyperaccumulators for Re with TF and BCF greater than one and ten, respectively. The results of this work should be further developed in order to confirm the potential use of these species in phytoextraction programs.

Keywords: *Soil Metal Concentration, Translocation Factor, Bioaccumulation Factor, Hyperaccumulation Plants.*

1. Introduction

Mining activities generate large volumes of tailings for millions of tons. Tailings are usually deposited on the surface in locations established within the mine area and can remain in these locations for many decades in a non-rehabilitated state. Tailings generally provide an undesirable substrate for plant growth due to their large concentrations of heavy metals, low pH, and small amounts of nutrients. These mine tailings became potential sources of pollution owing to water and wind erosion. Efforts to restore a vegetation cover can benefit stabilization, pollution control, and improve aesthetical aspects [1-3]. Heavy metals are currently of environmental concern owing to their durability and toxicity. Hence, heavy metals pose risks to food production and human health [4]. Various technologies have been developed to remediate the heavy metal contamination of soil in order to protect the environment. However, most of them are costly and in many cases result in significant secondary damage to the environment [5].

Phytoextraction is a new technology for remediation of heavy metal-contaminated sites [6]. This method involves growing heavy metal-tolerant plants with the potential to take up and concentrate heavy metals from soils into the plant tissue during their metabolic process to phytoremediate potentially harmful contaminants [7]. Plants with high biomass and the capability to accumulate appropriate amounts of heavy metals prepare this purpose [8].

Phytoextraction can be considered in two main scopes: (a) phytoremediation, in which metal contaminants are stabilized or recovered for safe disposal [9] and (b) phytomining, in which precious metals such as gold (Au), platinum (Pt), and thallium (Tl) are extracted via cropping for commercial purposes [10, 11]. There has been a persistent interest on looking for native plants that are tolerant towards heavy metals [9]. However, few studies have evaluated the phytomining and phytoextraction potentials of native plants under field conditions. Heavy metals can cause intense phytotoxicity, and may act as a powerful force for the evolution of tolerant plant populations. Hence, it is possible to identify metal-tolerant plant species from natural plants in the field sites that are contaminated with various heavy metals [12].

In Iran, there are several metal mines, and the process of metal mining has led to intense heavy metal pollution [13]. Sarcheshmeh copper mine is the biggest metal mine in Iran located southeast of Iran. Our investigation focused on identifying the metal-tolerant plant species growing on the tailings site of this copper mine. The aims of this work were to (1) demonstrate the concentrations of Re, Cu, Mo, Ni, Zn, and As in the plant species growing spontaneously on a contaminated site and (2) determine the feasibility of using these plant species for phytoextraction and phytomining.

2. Materials and method

2.1. Site description and sample collection

The Sarcheshmeh porphyry copper deposit, the most important open-pit copper mine in Iran, is located in the central Iranian volcano–plutonic copper belt, about 160 km SW of Kerman, SE of Iran. This deposit has been distinguished to be the fourth largest porphyry copper mine in the world, and has been evaluated to consist of 1 billion tons of copper (0.9%) and about 30 times less for Mo (0.03%) [14].

The Sarcheshmeh deposit occurs in the southern segment of the central Iranian volcano plutonic belt composed of subduction-related calc-alkaline [15] and adakitic rocks [16]. The mineralization of the deposit is related to granodiorite stock [17] intruding into a folded and faulted early Tertiary volcano-sedimentary series containing andesitic lavas, tuff, ignimbrite, and agglomerate [18]. At the deposit scale, the ore body is elliptical in shape with a length of about 2,300 m and a width of about 1,200 m. Open-pit mining has been operating for more than 30 years, and a notable amount of low-grade waste dumps and tailings have been produced by mining activity and mineral processing operations, which can cause environmental problems [19]. As a result, each year, approximately 10,000 tons of waste and 1,215,000 tons of tailings are produced with an average grade of 0.6% and 0.1% Cu, respectively, in the Sarcheshmeh ore processing plants [20].

Exceeding 20 Mt of tailings have been produced and deposited in the natural valleys about 25 km north of the mine in a mountainous area at 2300 m above the sea level. [21]. The tailings site occupies an area of about 11 km^2 and its average depth was approximately 60 m in 2015 (Figure 1). The annual average of the total precipitation is around 300 mm to 550 mm, and the average temperatures in this area in summer and winter are about 35 °C and −20 °C, respectively [22].

According to our observation, seven plant species grow well and are dominant in the surface area of Sarcheshmeh tailings site. Plant samples together with the associated soil in the tailings site were collected in August 2015. The studied species included 4 families, of which 3 species belonged to Chenopodiaceae, forming the predominant ingredient in this site, and 2 species belonged to Poaceae (Table 1). At least, three samples of each studied species were randomly prepared within the sampling area. Soil samples near the roots of plants were also taken in the studied area at a depth of 0–20 cm, with foreign objects removed. At each plant species, soil samples were combined entirely to form a composite sample. Plant samples were kept in paper bags, while soil samples were stored in plastic bags for transport to the laboratory.

Table 1. Family and species composition of plant samples in tailings site of Sarcheshmeh mine.

Species No.	Scientific name	Family
1	Arundo donax L. - Giant reed	Poaceae
2	Tamarix ramosissima L. - Saltcedar	Tamaricaceae
3	Salsola kali L. Russian thistle	Chenopodiaceae
4	Cynodon dactylon (L) Pers.- Bermudagrass	Poaceae
5	Chenopodium album L. - Lambsquarters	Chenopodiaceae
6	Atriplex leucoclada Boiss.	Chenopodiaceae
7	Zygophyllum fabago L. - Syrian beancaper	Zygophyllaceae

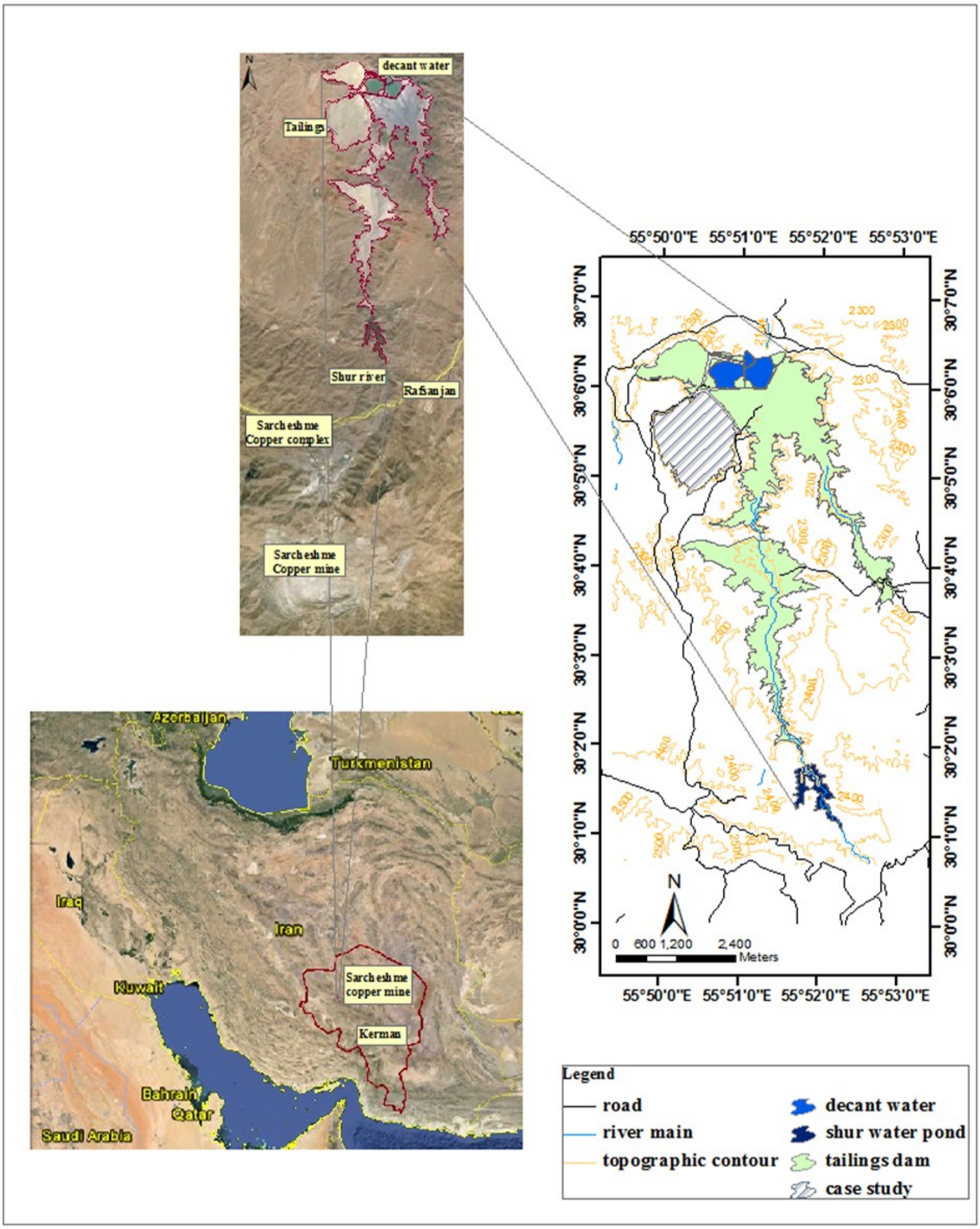

Figure 1. Satellite image and topographic map of Sarcheshmeh copper mine and tailings site.

2.2. Soil and plant analysis

The collected soil samples were air-dried for a week and then crushed to the particles lower than 0.3 cm in diameter. The soil samples were analyzed for pH, organic matter, electrical conductivity, and available N, P, K, and particle size fractions. The soil pH and electrical conductivity (EC) were measured in 1:2 soil:deionized water suspension triplicates using a glass electrode pH-meter and an EC-meter, respectively. The available N, P, K, and percent organic carbon were analyzed using the standard methods [23, 24]. Soil texture was defined by the pipet method [25].

For determination of the trace element content, approximately 1 g of the dried and ground soil sample was digested using 4 mL of nitric acid (63%) and 12 mL of hydrochloric acid (37%) in a beaker at 80 °C for 2 h. The solution was filtered and transferred to a 100-mL volumetric flask. The concentrations of As, Cu, Ni, Zn, Mo, and Re were determined by an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP/OES) using a AMETEK Spectro Arcos FHX ICP in Sharif University of technology, Iran.

All plant samples were divided into shoots and roots, which were thoroughly washed with tap water and rinsed with deionized water to eliminate entirely the soil particles attached to the shoot and root surfaces. After rinsing, the plant samples were air-dried at room temperature (25 °C) for three days, and then separately oven-dried in paper bags at 50 °C for 48 h. The dried samples were ground into fine powders by a stainless steel mill. Finally, 1 g of a dry sample was digested with an acidic mixture of 3:1 conc. HCl:conc. HNO_3 (aqua regia) in a beaker, and then the mixture was heated at 80 °C for 4 h. The solution was filtered and transferred into a 50-mL volumetric flask for analysis.

2.3. Calculations and data analysis

The ability of plants to tolerate and accumulate heavy metals can be quantified by calculating the bioconcentration factor (BCF) and the translocation factor (TF). The plant BCF represents the efficiency of a plant in accumulating a metal into its tissues from the surrounding environment. It is calculated by the following equation:

$$BCF = \frac{metal\ concentration\ in\ the\ plant;\ mg\,kg^{-1}}{metal\ concentration\ in\ the\ soil;\ mg\,kg^{-1}} \quad (1)$$

TF reflects the efficiency of the plant species in translocating the accumulated metals from its roots to shoots. It is calculated according to the following equation [26-28]:

$$TF = \frac{metal\ concentration\ in\ the\ shoots;\ mg\,kg^{-1}}{metal\ concentration\ in\ the\ roots;\ mg\,kg^{-1}} \quad (2)$$

The data is presented as mean and standard deviation. All statistical analyses were performed using the SPSS (Statistic Program for Social Sciences) statistical program package, version 24 [29] (and Microsoft excel, version 2016 [29]).

3. Results and desiccation

3.1. Soil properties and trace element concentration

The soils from the different plant samples showed acidic pH values with an average value of 4.65. The average electrical conductivity (EC), organic carbon (OC), available nitrogen (N), phosphorous (P), and potassium (K) were detected to be about 12.26 ± 3.06 mS cm^{-1}, 0.26 ± 0.16%, 22.08 ± 6.31, 6.6 ± 5.64, and 214.75 ± 104.01 mg kg^{-1}, respectively. Also soil texture was silty loam in the soil collected from the tailings site of this mine.

Analysis of soil samples revealed high concentrations of As, Cu, Mo, Ni, Zn, and Re (Table 2). The average values for As, Cu, Mo, Ni, Zn, and Re were 18.44 ± 13.41, 1280 ± 500.95, 25.06 ± 13.33, 32.9 ± 14.39, 251.82 ± 95.82, and 1.7 ± 0.78 mg kg^{-1}, respectively. Among all the heavy metals and As analyzed in the soil samples, the average concentration of Re was the lowest, followed by As, Mo, Ni, Zn, and Cu. The highest As and Cu contents were 47.65 and 2138.0 mg kg^{-1}, respectively, and both metals were detected in a sample collected from the *A. donax* species. The highest Mo, Ni, and Re contents were 47.3, 46.10, and 3.33 mg kg^{-1}, and these metals were detected in a sample collected from *C. album* species. The highest Zn content was 343.18 mg kg^{-1}, and this metal was detected in a sample collected from the *A. leucoclada* species. Jannesar Malakooti et al. [21] have reported the As, Cu, Mo, Ni, and Zn concentrations to be 20.97 ± 2.3, 1366 ± 123.61, 104.49 ± 12.46, 26.15 ± 1.9, and 166.33 ± 7.32 mg kg^{-1}, respectively, for the Sarcheshmeh tailings. In another study, concentrations of Cu, Ni, and Zn have been reported to be 130-400, 26-34 and 90-250 mg kg^{-1}, respectively, in the tailings site of this mine [30].

According to the Canadian Environmental Quality Guidelines (CEQGs) [31], we found that the mean As and Cu contents (18.44 ± 13.41 and 1280 ± 500.95 mg kg^{-1}) exceeded the limits for agricultural and industrial land use, and also Mo and Zn mean values (25.06 ± 13.33 and 251.82 ± 95.82 mg kg^{-1}) were higher than the limits for agricultural soil. As a result, these findings corresponded to a serious pollution. On the other hand, according to Kabata and Pendias [32], the highest concentrations of As, Cu, Mo, and Zn in the soil samples were higher than the standard limits of heavy metals and As in agricultural soil by values of 20, 150, 10, and 300 mg kg^{-1}, respectively.

Table 2. Total concentration (mg kg^{-1}) of heavy metals and As in soil and mean concentrations (mg kg^{-1} dry weight ± standard deviation) of heavy metals and As in shoots and roots of plants growing at tailings site of Sarcheshmeh copper mine.

		As	Cu	Mo	Ni	Zn	Re
A. donax	Soil	**47.65**	**2138.00**	31.65	44.00	172.10	1.05
	Root	0.26 ± 0.18	8.41 ± 2.72	0.03 ± 0.03	1.95 ± 1.56	24.42 ± 2.35	0.09 ± 0.05
	Shoot	6.35 ± 0.8	42.54 ± 3.47	0.3 ± 0.25	22.12 ± 6.92	144.3 ± 10.02	23.08 ± 4.2
T. ramosissima	Soil	11.40	743.00	14.00	16.20	200.30	1.50
	Root	2.91 ± 0.71	**160.7 ± 38.07**	6.23 ± 1.56	18.08 ± 4.14	106.82 ± 20.6	14.21 ± 3.53
	Shoot	19.79 ± 3.36	**454.39 ± 102.96**	30.85 ± 7.71	**45.54 ± 5.86**	495.77 ± 87.87	64.61 ± 10.38
Salsola kali	Soil	8.70	1278.00	35.50	41.90	313.40	1.29
	Root	22.36 ± 7.16	132.76 ± 38.43	5.18 ± 1.43	71.02 ± 18.2	468.25 ± 149.86	89.17 ± 28.5
	Shoot	**23.89 ± 9.2**	95.49 ± 6.1	40.03 ± 3.99	5.32 ± 3.55	514.53 ± 111.23	339.57 ± 93.7
C. dactylon	Soil	11.00	669.00	14.20	16.60	211.36	1.50
	Root	10.29 ± 0.18	152.54 ± 36.38	**27.19 ± 5.32**	34.83 ± 28.73	215.81 ± 59.88	44.38 ± 4.76
	Shoot	19.37 ± 3.61	247.5 ± 49.62	56.95 ± 18.25	30.3 ± 3.34	794.37 ± 110.29	100.14 ± 10.98
C. album	Soil	20.20	1320.00	**47.30**	**46.10**	298.00	**3.33**
	Root	**24.28 ± 6.91**	154.28 ± 5.82	5.31 ± 0.23	**89.24 ± 19.83**	**550.11 ± 137.21**	**97.68 ± 24.27**
	Shoot	13.84 ± 3.62	109.31 ± 5.26	39.1 ± 7.06	26.67 ± 4.1	477.51 ± 86.19	89.86 ± 23.92
A. leucoclada	Soil	14.50	1599.00	12.60	45.40	**343.18**	2.14
	Root	7.96 ± 1.69	51.56 ± 16.04	6.79 ± 0.33	30.61 ± 5.75	194.56 ± 57	33.94 ± 9.41
	Shoot	19.93 ± 2.5	193.96 ± 0.18	145.53 ± 5.28	22.16 ± 22.05	753.76 ± 88.07	**520.78 ± 131.94**
Z. fabago	Soil	15.60	1213.00	20.20	20.10	218.95	1.36
	Root	6.04 ± 1.73	68.34 ± 22.82	14.37 ± 3.85	23.67 ± 6.16	185.17 ± 50.4	24.67 ± 5.76
	Shoot	15.03 ± 3.38	189.66 ± 21.03	**82.93 ± 12.1**	31.96 ± 1.31	**1233.58 ± 411.43**	286.12 ± 34.43

3.2. Metal concentrations in plants

Metal concentrations in plants vary with the plant species [33]. Heavy metal and metalloid uptake by plants happens either with the mass flow of water into the roots passively or via active transport through the plasma membrane of root epidermal cells from soil. Plants can possibly concentrate most metal ions for at least an order of magnitude greater than in the surrounding medium in normal growing conditions [26]. Ultimately, the total concentration and chemical forms of trace elements in the soil controlled their bioavailability to plants. A combination of low pH and high concentration of heavy metals and metalloids in soil lead to high plant uptake of heavy metals and metalloids [34].

In this work, a total of 30 plant samples of 7 species was collected from the surface of Sarcehshmeh tailings site. Plants growing in this area accumulated a considerable amount of heavy metals and As in both shoots and roots, regardless of the species (Table 2).

The total As concentrations in the plant shoots differed among the species at the polluted site from 6.35 mg kg^{-1} to 23.89 mg kg^{-1}, and in roots from 0.26 mg kg^{-1} to 24.28 mg kg^{-1}, with the maximum content in the shoots of *Salsola kali* and roots of *C. album*. The As content in the shoots of these plants was clearly smaller than the threshold value used to regard plants as hyperaccumulators (i.e. 1000 mg kg^{-1}) [35]. The results indicated As concentration in the shoots of plants with the exception of C. Album was slightly higher in their roots. Hence, the As content of shoots in the studied species was less efficient than those published by Bech and Lansac [36] for *Paspalum tuberosum Mez* and *Paspalum racemosum Lam.* (1130 and 1530 mg kg^{-1}, respectively); however, in another study, Bech et al. [37] have reported that *Ageratina sp.* and *Epilobium denticulatum* absorbed up to 286.5 and 298.3 mg kg^{-1} of As, respectively, in a polymetallic mine (mainly Ag, Pb, and Cu) of Cajamarca Province in Peru. Nevertheless, arsenic is neither essential nor beneficial to plant nutrition, and is normally present at about 1–1.7 mg kg^{-1} in plant tissues [32]. In view of this, As concentration in the whole plant species clearly exceeded the normal level.

The total copper concentrations in the plant samples collected from the site were variable, ranging from 42.54 mg kg^{-1} to 454.39 mg kg^{-1} in shoots and 8.41 mg kg^{-1} to 160.7 mg kg^{-1} in roots, the maximum Cu concentrations in both shoots and roots of *T. ramosissima*. The Cu content in the shoots of the plants presented was smaller than the threshold value used to regard plants as hyperaccumulators (i.e. 1000 mg kg^{-1}) [35]. Despite the small translocation of copper from roots to shoots naturally, most species show different behaviors in aerial parts with a higher concentration of Cu than roots. Copper is also essential to plant growth but will cause toxic effects when shoots or leaves concentrate Cu amounts more than 20 mg kg^{-1} of Cu [38]. The majority of Cu values in this research work were high.

Moreover, these values were much greater than those reported for similar species including *A. donax* (2 mg kg^{-1}), *Tamarix sp.* (20 mg kg^{-1}), *Salsola kali* (36 mg kg^{-1}), *Atriplex sp.* (63 mg kg^{-1}), and *Peganum harmala L.* (Zygophyllaceae) (30-36 mg kg^{-1}) from this studied area by Ghaderian and Ravandi [30]. Cu concentrations in the range of 37.7-542.3 mg kg^{-1} in plant shoots were reported by Bech et al. [37]. Analyzing the Cu concentration in plants collected from a mining site, Wan et al. [39] showed similar Cu concentrations in *Pteris vittata L.* and *Viola principis H. de Boiss.* (380.7and 210.8 mg kg^{-1}, respectively). Ha et al. [40] have reported a range of 8.56-87.5 mg kg^{-1} of Cu concentration in different plant species at one of the largest lead-zinc mines in Northern Vietnam.

Total Mo concentrations in the plant shoots ranged from 0.3 mg kg^{-1} to as high as 145.53 mg kg^{-1}, and in plant roots from 0.03 mg kg^{-1} to as high as 27.19 mg kg^{-1}, with the maximum level in the shoots of *A. Leucoclada* and roots of *C. dactylon*. These results indicated that Mo concentrations in the shoots of all plants were higher than their amount in roots. The toxic concentrations of Mo are considered to be 10-50 mg kg^{-1} in plant tissues [32]. Thus the collected plant species of *C. dactylon*, *A. Leucoclada*, and *Z. fabago* showed concentrations higher than this toxic level for Mo in their root and shoot tissues.

Zinc is an essential element to all plants, and is normally present at concentrations of 27-150 mg kg^{-1}, and its toxic level is between 100 and 400 mg kg^{-1}. On the other hand, hyperaccumulation of Zn by plants is extremely rare, as it tends to precipitate as insoluble sulfate in the rhizosphere. Therefore, the potential uptake and transport to the aerial parts of the plants will be minimized [35, 41]. The total zinc concentrations in the plant shoots differed among the species in this work from 144.3 mg kg^{-1} to as high as 1233.58 mg kg^{-1}, and in roots from 24.42 mg kg^{-1} to as high as 550.11 mg kg^{-1}, with the maximum content in the shoots of *Z. fabago* and roots of *C. album*. Nevertheless, all the plants grow at this site with the exception of C. Album was able to accumulate more Zn in shoots than in roots, none of which absorbed up to 10000 mg kg^{-1} of Zn in their shoot tissues. According to the results of this research work, these plants cannot be considered as Zn hyperaccumulators [35]. The ranges of Zn in the plant tissues presented here were generally higher than the toxic levels reported for the plant species. These values were greater than those reported by Ghaderian and Ravandi [30] for the plant species in this studied mine (from 3 to 111 mg kg^{-1}) but less than those of the specific hyperaccumulator *Noccaea caerulescens* (J. Presl & C. Presl) F.K. Mey, which is able to concentrate approximately 10,000 mg kg^{-1} of Zn [42, 43]. Bech et al. [44] reported the great capacity of *P. orbignyana* growing in mine areas to transport zinc from roots (3100 of Zn mg kg^{-1}) to the aerial parts (9600 of Zn mg kg^{-1}); although they published that *Ageratina sp.* and *E. denticulatum* were able to concentrate approximately 12000 and 16000 of Zn mg kg^{-1}, respectively, in their studied site [37]. Zn concentrations of 53–1458 mg kg^{-1} reported by Lorestani, Cheraghi [45] in industrial site has shown a similar range with plant species found in this work.

The greatest number of hyperaccumulators recognized for Ni results from its relative availability in plants. More than 400 such Ni hyperaccumulators have been documented in the world, and all of these plants have been collected from serpentine soils [46]. The total Ni concentration in the plant shoots ranged from 5.32 to 45.54 mg kg^{-1}, and for plant roots from 1.95 to 89.24 mg kg^{-1}, with the maximum level in the shoots of *T. ramosissima* and roots of *C. album*. The results obtained illustrated that the Ni content in the shoots of all plants was clearly smaller than the threshold value used to consider plants as hyperaccumulators (i.e. 1000 mg kg^{-1}) [35]. Ha et al. [40] reported that the Ni concentration in all plants collected on the mine sites in Northern Vietnam was low with values from 0.49 to 81.9 mg kg^{-1} in shoots. On serpentine soils, Van der ent et al. [47] identified *Phyllanthus cf. securinegoides* as one of the highest globally Ni hyperaccumulation up to 2.3% in Sabah

(Malaysia). Furthermore, Ghaderian and Ravandi [30] found Ni concentrations of 0.6, 0.3, 3.5, 1.2, and <0.1-1.5 mg kg^{-1} in *A.donax*, *Tamarix sp.*, *Sal*sola kali, *Atriplex sp.*, and *Peganum harmala L.* (Zygophyllaceae), respectively, which is clearly lower than what has been recorded in the present work.

The total Rhenium concentrations in the plant shoots ranged from 23.08 mg kg^{-1} to as high as 520.78 mg kg^{-1}, and in plant shoots from 0.09 mg kg^{-1} to as high as 97.6 mg kg^{-1}, with the maximum level in the shoots of *A. Leucoclada* and roots of *C. album*. The results obtained indicated that the shoots of all plants could accumulate a more significant amounts of Re than the roots. Due to the great mobility and solubility of rhenium in the form of ReO_4^-, the most stable chemical form of Re, it is relatively easily available to plants in amounts exceeding many times its natural occurrence (the average from 0.0004 to 0.0006 mg kg^{-1}). So far, high concentrations of Re are preferably uptaken and translocated from roots to the aboveground parts of plants in ore dressing and metalliferous soils [48]. In the previous studies, Bozhkov et al. [49] reported an Re concentration of 1686 mg kg^{-1} ash weight in leaves of acacia growing in the copper mine site, while Shacklette, Erdman [50] showed the range of Re concentration as 70 to 300 mg kg^{-1} ash weight in native vegetation of the United States, both lower than those reported in our work. Therefore, the previous investigations indicate that the rhenium content in plants from ore deposit and mining regions exceeds many times its concentration in plants from ecologically normal regions. The plants enriched in rhenium can be considered as a source for rhenium production.

Van der Ent et al. [5] have proposed to set the hyperaccumulation threshold criteria at a minimum of 2–3 orders of magnitude higher than in plant tissues on normal soils, and at least one order of magnitude greater than the range in plant tissues on metalliferous soils. They have proposed that the criteria for hyperaccumulation of Cu and Zn be lowered to 300 and 3,000 mg kg^{-1} dried plant leaf. Based on this concept, the criteria for hypperaccumulation of Re can be considered 100 mg kg^{-1} dried plant leaf. As it was pointed out by Van der Ent et al. [5], the data presented in this work indicates that the hyperaccumulation levels were obtained for *T.ramosissima* for Cu and *Salsola kali*, *C. dactylon*, *A. Leucoclada*, and *Z. fabago* for Re. Nevertheless, these species must be confirmed as Cu and Re hyperaccumulators in further glasshouse experiments. In contrast, in this work, the lowest potentially accumulate heavy metals and As has been identified by *A. donax* among the sampled plants that exhibited minimum concentrations of As, Cu, Mo, Ni, Zn, and Re in both the root and shoot tissues. In addition, all plant species were able to adapt efficiently to grow in mine-impacted soils and tailings. These results may indicate that the plant species grown on the present site are tolerant of the mentioned heavy metals and As.

3.3. Bioaccumulation and translocation in plants

In this work, we focused not only on the total concentrations of heavy metals and As in plant species tissues but also on the bioaccumulation and translocation factors that were computed as they could be considered to define the hyperaccumulator plant species. In particular, hyperaccumulators have an extremely high bioconcentration factor (shoot:soil ratio) as a result of their physiological structure enabling active metal sequestration and accumulation, and it has been proposed that this should be a exigent factor involved in the identification of hyperaccumuators [51]. On the other hand, the process of phytoextraction usually requires the plant species that have a strong ability to translocate metals from roots to the easily harvestable plant parts, i.e. shoots [12]. Another criterion that has been proposed for defining hyperaccumulation is the shoot-to-root ratio of metal concentrations (translocation factor). For a classification viewpoint, TF > 1 indicates that the plant translocates metals effectively from root to shoots; BCF >10 infers the hyperaccumulator species, BCF > 1 shows the accumulator species, and BCF < 1 represents the excluder species [52].

The translocation factor showed that the plants most efficiently translocated metals to their aerial parts (Figure 2). The results of this work indicated the As, Zn, and Re concentrations in all of the plant species shoots, except for *C. album*, were substantially greater than those in roots (Table 2). However, these plant species were highly efficient in taking up and translocating As, Zn, and Re (TF of 1.05 ± 0.08 to 36.04 ± 29.98, 1.13 ± 0.13 to 6.58 ± 0.45, and 2.26 ± 0.01 to 307.78 ± 145.53, respectively). The TF values for Cu were greater than one for all the studied plants, except for *Salsola kali* and *C. album* at this site. The Ni concentrations in the shoots were greater than those in the roots for *A. donax*, *T. ramosissima*, *C. dactylon*, and *Z. fabago* with the TF values of 15.19 ± 7.580, 2.56 ± 0.27, 1.42 ± 1.13, and 1.41

± 0.32, respectively. However, the TF values less than one for *Salsola kali*, *C. album*, and *A. leucoclada* presented less efficiency in taking up and translocation of Ni in their shoots. All the studied plants also showed efficient Mo translocation with TF values ranging from 2.06 ± 0.27 to 21.48 ± 1.280. Therefore, *A. donax*, *T. ramosissima*, *C. dactylon*, and *Z. fabago* grown at the studied site had greater TF values for all elements. To the contrary, the low TF values were reported in *C. album* for all elements excluding Mo, *Salsola kali* for Cu and Ni, and *A. leucoclada* for Ni.

BCF for metals and metalloid has been descripted in Figure 3. The As concentration in shoots of *T. ramosissima, Salsola kali, C. dactylon*, and *A. leucoclada* were greater than that in the tailings soils, as a result of BCF values being higher than one, while *A. denox*, *C. album*, and *Z. fabago* had BCF values less than one for As. None of the plant species showed BCF values greater than one for Cu (0.61 ± 0.14 to 0.02 ± 0.00) because the soil Cu concentration in this site was relatively high, at mean of 1280 ± 500.95 mg kg^{-1}. *A. leucoclada* presented the highest BCF value of Mo for 11.55, and also the *T. ramosissima*, *Salsola kali,* C. dactylon, and Z. fabago species grown at this site had BCF values greater than one, relative to the other species. Most plant species also exhibited large Zn values in shoots. Among the plants grown at the site, only *A. donax* had a TF value lower than one for Zn. In other studies, Bech et al. [37] reported BCF values < 0.5 for the plant species grown in the polluted sites for As, Cu, and Zn. The BCF as high as 5.7 was reported for Zn in plants of the polymetallic Carolina mine by Bech et al. [44], while the BCF value for As was recorded to be less than 0.4. However, in both studies, the metal soil concentrations were larger than in the soils of the present work. Surprisingly, all the plant species were mainly most efficient in taking up Re and concentrating in shoots higher than in tailings soil value. So far, this interaction has brought about BCF values higher than 10 (ranging from 21.98 to 264.05).

Based on this result, most plant species from this area were extremely efficient in taking up and translocating metals and metalloids. In spite of the plant ability to translocate metals from underground parts to the aboveground tissues, the concentration of most metals in these plants is lower than the hypperaccumulation threshold (e.g. the root of *A. donax* can maintain no metals and metalloids in its tissues, and entirely translocates the metal absorption to the shoot tissues. Therefore, the TF values were greater than one, while the BCF values for metals were generally less than one).

Generally, Re is highly available for plants than the other trace metals that have a spatial potential to be absorbed to the underground tissues and be translocated to shoots in a larger concentration than its substrate. Among those plant species collected from the contaminated site, *Salsola kali*, *C. dactylon*, *A. leucoclada*, *and Z. fabago* can be considered the hyperaccumulators of Re, according to the following criteria: they were able to accumulate more than 100 mg kg^{-1} of Re in their shoots [53, 54] and had TF and BCF values for Re greater than one and ten, respectively [55].

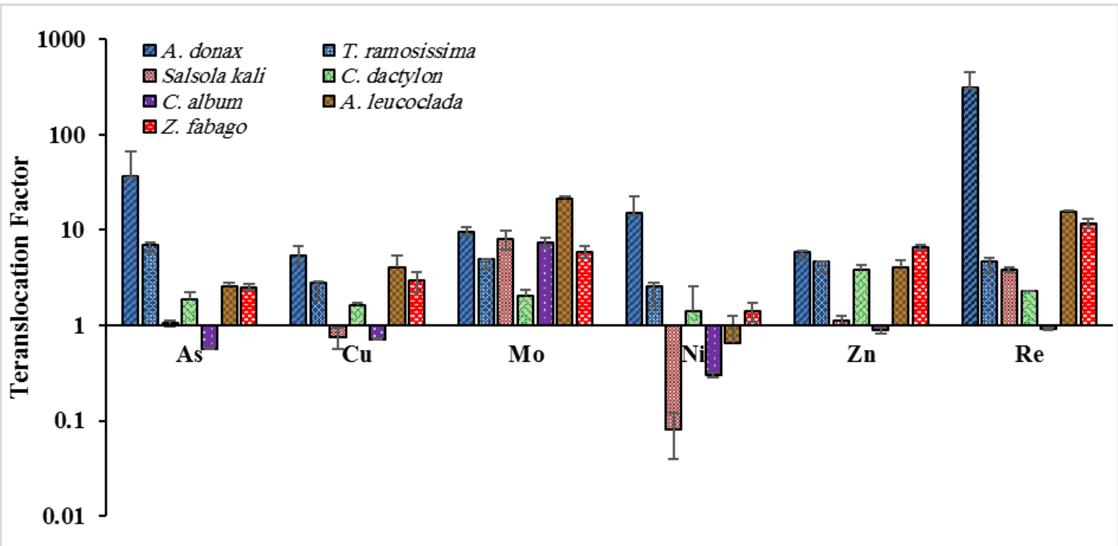

Figure 2. TF for heavy metals and As in plant species growing at Sarcheshmeh copper mine tailings. Values in each column represent mean ± standard deviation. Error bars show standard deviations.

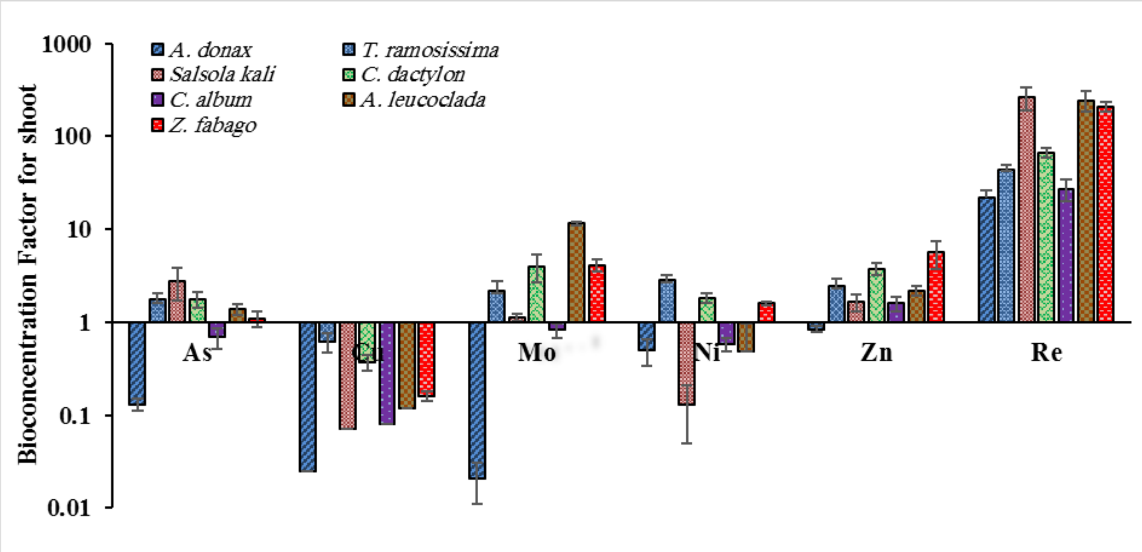

Figure 3. BCF of heavy metals and As in plant species collected from tailings site of Sarcheshmeh Copper mine. Values in each column represent mean ± standard deviation. Error bars show standard deviation.

BCF > 1 and TF > 1 were recorded for Zn, Mo, and As in *T. ramosissima*, *C. dactylon*, *A. leucoclada*, and *Z. fabago* and for Ni in *T. ramosissima*, *C. dactylon*, and *Z. fabago*, while the concentration of these metals were lower than the hypperaccumulation threshold (Table 2). These species can be considered for remediation and environmental purposes. Finally, *T. ramosissima* could be the most promising species for phytoextraction of Cu since it was able to accumulate more than 300 mg kg^{-1} of Cu in shoots and had a TF value greater than one. However, the BCF index was smaller than one, which may be attributed to the large Cu concentration in the soils (mean of 1280 ± 500.95 mg kg^{-1}). Similar results were obtained by Reeves [42], who suggested that this index was not a reliable tool for classification purposes. Nonetheless, a decisive taxonomy of these plants as metal hyperaccumulators requires more studies applying cultivation in hydroponics and controlled environment.

4. Conclusions

Based on this work, most of the species grown in the tailings site of Sarcheshmeh copper mine have an admirable ability to transport metals and metalloids from the roots to the shoots, especially for Re. In this site, *T. ramosissima*, *C. dactylon*, *A. leucoclada*, and *Z. fabago* could strongly tolerate and extremely accumulate multiple metals; based on these characteristics, these plants can be considered as candidates for the phytoextraction of multi-metals in contaminated areas. It could be suggested that *T. ramosissima* could be suitable for phytoextraction of Cu due to its ability to accumulate more than 300 mg kg^{-1} of Cu in the shoots, with TF greater than one. It seems that BCF is not a reliable index when the metal soil concentration is extremely large. Moreover, *Salsola kali*, *C. dactylon*, *A. leucoclada*, and *Z. fabago* can be considered as the most promising species for phytoextraction of Re in this site. These species should be cited as the possible hyperaccumulators of Re with the TF and BCF values greater than one and ten, respectively. Based on the results obtained from this work, the concentration of rhenium accumulated by these plants were so high that it could be concluded that phytomining of Sarcheshmeh tailings would be an economically viable operation. To fully investigate the potential for phytomining and phytoextraction, further studies (both greenhouse and field experiments) are required to confirm the phytomining and phytoextraction potentials of the plants present as well as to establish their agricultural requirements and optimal management practices.

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مطالعه پتانسیل استخراج گیاهی و گیاه معدنی رنیوم و فلزات سنگین بر روی گیاهان رشد یافته بر سطح رسوبات باطله فرآوری معدن مس سرچشمه، جنوب شرق ایران

سمیرا طبسی، حسین حسنی* و امیر رضا آزادمهر

دانشکده مهندسی معدن و متالورژی، دانشگاه صنعتی امیرکبیر، ایران

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* نویسنده مسئول مکاتبات: hhassani@aut.ac.ir

چکیده:

شناسایی و بررسی ویژگی‌های گونه‌های گیاهی مقاوم به فلزات سنگین با توانایی استخراج گیاهی، رشد یافته بر سطح رسوبات باطله فرآوری معدن مس سرچشمه در جنوب شرق ایران، هدف این مطالعه است. غلظت فلزات AS، Cu، Mo، Ni، Zn و Re در خاک و بافت گیاهان شامل اندام هوایی و ریشه به طور جداگانه با کمک ICP-OES اندازه‌گیری شد. غلظت متوسط AS، Cu، Mo، Ni، Zn و Re در خاک به ترتیب 18.44±13.41، 1280±500.95، 25.06±13.33، 32.9±14.39، 33، 251.82±95.82 و 1.7±0.78 میلی‌گرم بر کیلوگرم برآورد شد. ضریب غنی‌شدگی زیستی و ضریب جایگیری برای ارزیابی میزان انباشت عناصر در اندام هوایی و ریشه هر یک از گونه‌های گیاهی و پتانسیل آن‌ها برای استخراج گیاهی محاسبه شد. بر اساس نتایج به دست آمده و مقایسه آن‌ها با استانداردهای موجود، گونه‌های گیاهی گز، مَرغ، آتریپلکس و قیچ با تحمل‌پذیری بالا قادر به انباشت چندفلزی در اندام خود می‌باشند. همچنین میزان ضریب غنی‌شدگی زیستی و جایگیری به ترتیب بیشتر از ۱ و ۱۰، گونه‌های گیاهی شور، مَرغ، آتریپلکس و قیچ را در دسته گیاهان بیش انباشتگر رنیوم قرار می‌دهد. با این وجود برای به کارگیری این گونه‌های گیاهی در برنامه‌های استخراج گیاهی نیاز به پژوهش‌های تکمیلی بیشتر اجتناب‌ناپذیر است.

کلمات کلیدی: غلظت فلزات در خاک، ضریب جایگیری، ضریب غنی‌شدگی زیستی، گیاهان بیش انباشتگر.