

## Bio-accumulation of major, trace, and rare earth elements by two *Astragalus* species grown on Agh-Dareh and Zarshouran gold deposits, Takab, NW Iran

S. Torbati<sup>1\*</sup>, S. Alipour<sup>2</sup>, M. Rostami<sup>2</sup> and S. Hajializadeh<sup>2</sup>

1. Department of Environmental Science, Urmia Lake Research Institute, Urmia University, Urmia, Iran

2. Department of Geology, Faculty of Science, Urmia University, Urmia, Iran

Received 21 April 2018; received in revised form 22 May 2018; accepted 30 May 2018

\*Corresponding author: s.torbati@urmia.ac.ir (S. Torbati).

### Abstract

The Agh-Dareh and Zarshouran mines are two known active gold deposits in Takab, NW Iran. In the present study, the potentials of two species of *Astragalus* (*A. microcephalus* from Agh-Dareh and *A. effusus* from Zarshouran mines), as the dominant plants grown in these areas, were assessed for the bio-accumulation of the major, trace, and rare earth elements (REEs). The plant and soil samples were collected from the mining areas and analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS). According to the results obtained, *A. effusus* in the Zarshouran mine passed a high ability in the accumulation of some major elements such as S, P, K, Ca, and Zn. Although the amounts of the examined trace elements in the soil samples were more than those in the shoots of both examined plants, the potential of *A. microcephalus* in the absorbance and translocation of Cd, U, Tl, and Pb was more than that for *A. effusus*. It became clear that the performance of *A. microcephalus* from the Agh-Dareh mine in the uptake and transportation of REEs was more than that for *A. effusus* from the Zarshouran mine; also both plant species absorbed and transported much more light REEs than heavy REEs did. According to the results obtained, the present study provides some geochemical findings about the substrate and leads to the increasing information about the plants as a useful indicator of metal mineralization.

**Keywords:** *Astragalus*, Bio-accumulation, Gold Deposits, Agh-Dareh, Zarshouran.

### 1. Introduction

Different activities such as mining and smelting of metal ores can lead to an increase in the concentration of metals in the environment; in fact, metal pollution has become one of the main concerns in many parts of the world [1]. Polluted environment can be remediated by different physical, chemical, and biological techniques [2]. Meanwhile, the use of green plants serving as some kind of bio-remediator can remove pollutants from the environment; it also seems to be cost-effective and environmentally friendly [1, 3-5]. One of the main strategies of phytoremediation is phytoextraction, which consists of plants taking up the contaminants such as heavy metals and accumulating these to extremely elevated levels in the shoots; in fact,

plants can uptake various elements from their substrate mainly through their roots. Although some of these elements are essential nutrients for them, in most cases, the high concentration of elements can be toxic for the plants [6, 7]. They can use two different strategies in response to such elevated concentrations: exclusion and accumulation [8, 9]. In fact, the plants can restrict the transportation of the elements to their shoots (excluder plants) or accumulate a high level of elements in their above-ground parts (accumulator plants). If the element concentration in the plant reflects its bio-available concentration in the soil, the plant is an "indicator" [8, 10, 11]. Therefore, the plants not only can be used for the bio-remediation of the polluted environments but

also some of them can be identified as a useful indicator of metal mineralization, thereby, contributing to mineral exploration [5, 12, 13]. A bio-geochemical survey may provide geochemical information about the substrate. For instance, the composition of the vegetation reflects the availability of an element for the plants and their ability to absorb, transport, and accumulate the element.

The Agh-Dareh and Zarshouran gold deposits, two main gold deposits in the Takab region in NW Iran, are hosted by carbonate-rich sedimentary rocks of Miocene and Upper Proterozoic–Lower Cambrian age, respectively [14]. They have been compared with the Carlin-type deposits [15, 16], and are referred to as sedimentary rock-hosted disseminated gold (SRHDG) deposits [14]. The mining activities in the two present areas date back to some hundreds of years ago [17, 18]. Long years of mining in these areas have produced and accumulated a large volume of pollutants, and there is few information about the environmental impacts of mining activities in these areas.

There are about 8000 plant species belonging to 150 families in Iran, with around 2000 numbers of them being native [12, 19]. *Astragalus* L., which is the largest genus of Fabaceae, is one of the largest genera among flowering plants (2500 annual and perennial species) [20]. It has been reported that in the moderately cold sub-mountain regions of the northern hemisphere and south America, many species of *Astragalus* are one of the main components of plant communities [21]. In the Takab mining area, *Astragalus* sp. is also one of the dominant plant genera, and the ancient name of the area, Tikan Tapa, refers to the predominant existence of *Astragalus* species in this region. Although there are numerous natural metal-contaminated soils in different mining areas, there is little information about the concentration of different elements in the native plants of Iran; also not much is known about the relationship between the element concentrations in the plants and different soils [12, 22]. In addition, there is almost no information regarding the environmental bio-geochemical behaviors of rare earth elements (REEs) in the soil-plant system in different areas of Iran. Thus the present study was carried out for the first time to address the environmental bio-geochemical behaviors of the major, trace, and rare earth elements in two main gold deposits of Iran.

The objectives of the present study were to investigate the bio-accumulation of different

major, trace, and rare earth elements from the soils of Zarshouran and Agh-Dareh mines by two *Astragalus* species grown natively on these mining areas and to calculate biological absorption coefficient (BAC) as an indicator for element absorptions by plants. Moreover, the potentials of *A. microcephalus* and *A. effusus* for the remediation of polluted soils were compared. Eventually, evaluation of these plants for the treatment of the soils was carried out in the present study.

## 2. Material and method

### 2.1. Studied area

The Agh-Dareh (36° 40' and 47° 1' E) and Zarshouran (36° 43' N and 47° 8' E) gold deposits are located in the Takab mining area, NW Iran (Figure 1) at the intersection of Urumieh–Dokhtar volcanic belt [23]. The Takab area with moderate summers and very cold winters has a semi-arid climate with the annual precipitation of the area being about 400 mm [17, 24].

### 2.2. Soil and plant sampling and preparation

The soil and plant samples were gathered from the areas about 2 Km<sup>2</sup> in and around the Agh-Dareh and Zarshouran mines (in five and three studied sites, respectively) during the spring, 2016. The aerial parts (shoot) of *Astragalus microcephalus* (Figure 2a) and *Astragalus effusus* (Figure 2b) were collected as two dominant *Astragalus* species in the Agh-Dareh and Zarshouran mines, respectively. In fact, five soil samples and five samples from the shoots of *A. microcephalus* in addition to three soil samples and three samples from shoots of *A. effusus* were collected in and around the Agh-Dareh and Zarshouran mines, respectively.

The soil samples were collected from the 20-40 cm depth around the root of the sampled plants. After drying in an oven at 100 °C for 3 h and sieving through a 2-mm grid, the samples were digested by a HCl-HNO<sub>3</sub>-H<sub>2</sub>O mixture at 95 °C for 1 h. The digests were analyzed using HP Agilent 4500 ICP/MS (USA) at Zarazma Co., Iran.

All the plant shoot samples were first washed with tap water, and later with distilled water; then they were dried at room temperature at 70 °C for 24 h. The dried plant samples were ashed by heating at 200 °C; the temperature was gradually increased to 500 °C over 2 h. The ashed samples were digested in HNO<sub>3</sub> for 1 h; then they were kept in a HCl-HNO<sub>3</sub>-H<sub>2</sub>O mixture for 1 h at 95 °C. Finally, all the ashed plant samples were analyzed by ICP-MS.

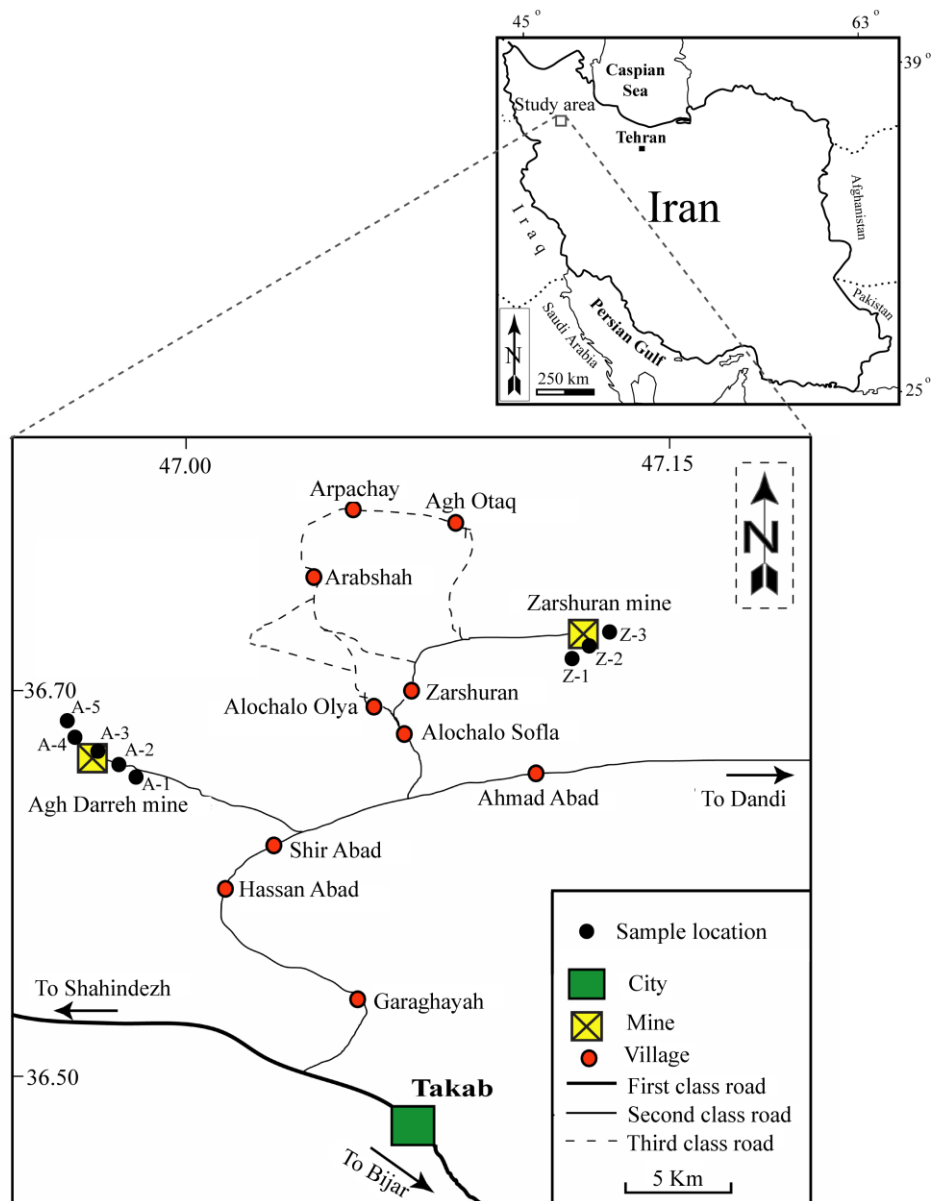


Figure 1. Location map of the studied areas.



Figure 2. a) *A. microcephalus* from Agh-Darch mine b) *A. effusus* from Zarshouran mine.

### 2.3. Biological absorption coefficient

In order to determine the absorption intensity of the plants from their substrates, the biological absorption coefficient (BAC) was calculated using Eq. (1) [25]:

$$\text{BAC} = C_p / C_s \quad (1)$$

where  $C_p$  is the concentration of an element in the plant ashes and  $C_s$  is the concentration of the same element in the soil samples.

## 3. Results and discussion

### 3.1. Accumulation of major elements

According to Figure 3, among the 11 elements studied as the major elements here (P, S, K, Ca, Al, Mg, Na, Fe, Zn, Ti, and Mn), only P was accumulated in the shoot of *A. microcephalus* was around 1.6 times more than that of the soil samples in the Agh-Dareh mine (Figure 3a). In contrast, *A. effusus* in the Zarshouran mine showed a high ability in the accumulation of some major elements such as phosphorus, sulfur, potassium, calcium, and zinc (near 9.6, 5.8, 3.7, 3.1, and 1.1-times more than those to the soil samples) (Figure 3b). Therefore, among the 6 main macronutrients (N, S, P, K, Ca, and Mg) essential for the plant normal growth, *A. effusus* could accumulate P, S, Ca, and K in its shoot more than the amounts of the soil. It could be concluded that between the two species of *Astragalus*, *A. effusus* had a good ability for

macronutrient absorbance and translocation to shoot, as compared to *A. microcephalus*.

P and S are two important macronutrients, without a sufficient amount of which, plants cannot normally grow. P forms about 0.2% of a plant's dry weight and S is found in the structure of the amino acids Cys and Met [26, 27]. In addition to these elements, Ca is one of the main plant nutrients required for different structural functions in the plant cell wall and membranes, and its cytosolic concentration is a main intracellular secondary messenger for organizing responses to numerous developmental signals and environmental challenges [28]. Moreover, plants require potassium ions for many indispensable roles such as a certain ionic environment for metabolic processes in cytosol, protein synthesis, movement of cells and organs, and activation of some enzymes [29]. According to the above-mentioned roles of these macronutrients in the normal growth of plants, the plants tendency to absorb high amounts of these elements is quite obvious. According to the results obtained, by comparing the accumulation manner of the plants with amounts of elements in the two groups of soils (Figure 4), *A. effusus* was also found to have a good potential for the absorbance and translocation of Fe and Mg from the soil of the Zarshouran mine, as compared to the absorption ability of *A. microcephalus* from the soil of the Agh-Dareh mine (Figure 4).

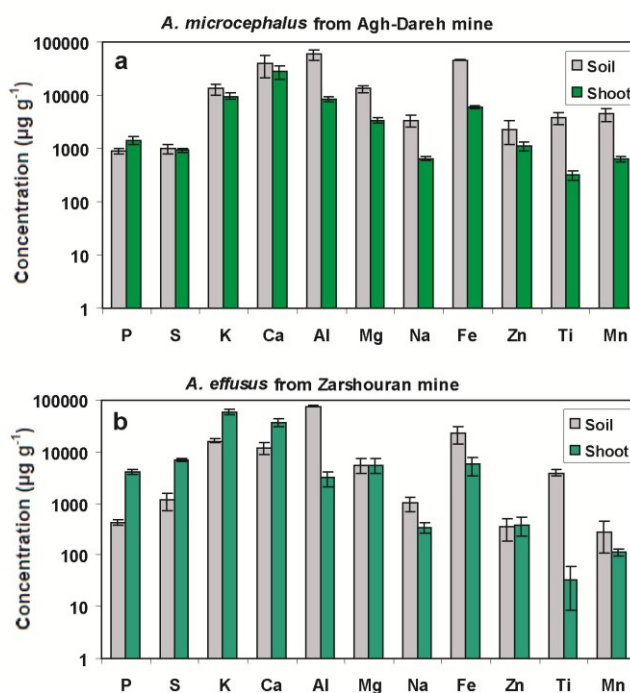


Figure 3. The amounts of major elements in the soils and shoot ashes of a) *A. microcephalus* from Agh-Dareh mine and b) *A. effusus* from Zarshouran mine (Mean  $\pm$  SE).

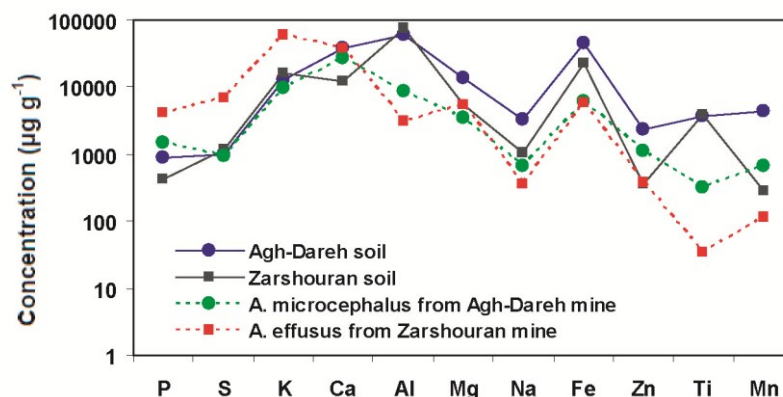


Figure 4. The trend of major element concentrations in the soils and shoot ashes of *A. microcephalus* from Agh-Dareh mine and *A. effusus* from Zarshouran mine.

### 3.2. Accumulation of trace elements

In order to determine the amount of trace elements in the soils of the two studied areas and in their plant samples, the contents of Cu, Mo, Cr, Co, Cd, Ni, U, Tl, Sr, V, and Pb were determined by the ICP-MS analysis. According to the results obtained, the amounts of the examined elements in the soil samples were more than those in the shoots of both plants (Figure 5). Figure 6 also compares the plants accumulation of the trace

elements with the contents of the elements in the two soil groups.

Accordingly, *A. microcephalus* was absorbed, transferring about 16.6, 24.5, 23.5, and 16.1 percent of the Cd, U, Tl, and Pb content of the soil of the Agh-Dareh mine, respectively. In fact, the potential of *A. microcephalus* in the absorbance and translocation of Cd, U, Tl, and Pb from the soil of Agh-Dareh was 3.2, 2.1, 4.6, and 6.2 times more than that of *A. effusus* regarding the mentioned elements, respectively (Figure 5).

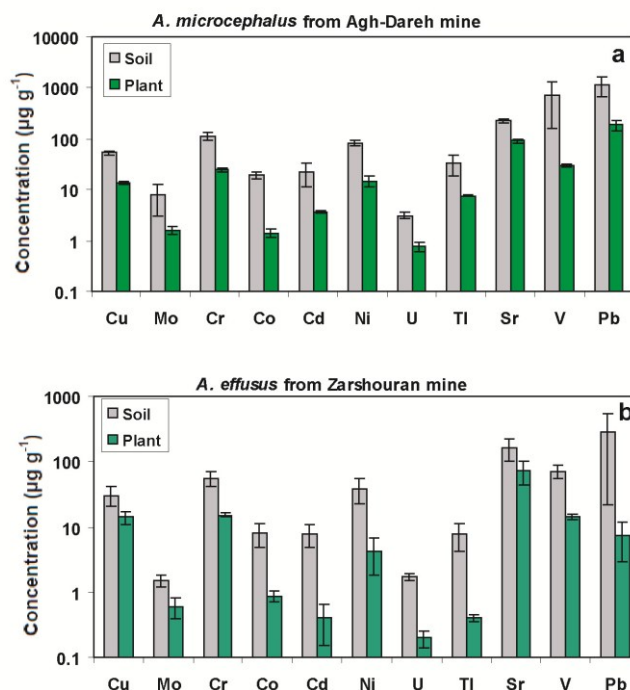
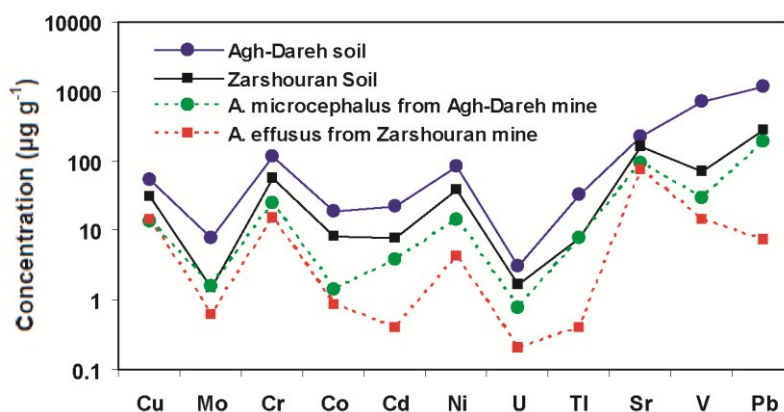


Figure 5. The amounts of trace elements in the soils and shoot ashes of a) *A. microcephalus* from Agh-Dareh mine and b) *A. effusus* from Zarshouran mine (Mean  $\pm$  SE).

The abundance of Cd in the Earth's crust averages  $0.1 \text{ mg kg}^{-1}$ . Meanwhile, the overall mean value of Cd in the world soils has been estimated to be  $0.41 \text{ } \mu\text{g g}^{-1}$  [30]. Soil contamination of Cd is believed to be the most serious health risk, and under the man-induced conditions, Cd is high in surface soils. For instance, the Cd concentration of surface soils in mining areas has been found to be in the range of  $2\text{--}400 \text{ } \mu\text{g g}^{-1}$  in different countries [30], and in the present study, its amount was 7.7 and  $22.2 \text{ } \mu\text{g g}^{-1}$  for the soils of the Zarshouran and Agh-Dareh mines, respectively (Figure 5). Therefore, the amount of Cd in the soils of the Zarshouran and Agh-Dareh mines was approximately 70 and 200 times more than that of Earth's crust, respectively. According to the

results of the previous studies, the Cd levels in legumes range from  $0.08$  to  $0.46 \text{ } \mu\text{g g}^{-1}$  in different countries, and this value is near  $4.9 \text{ } \mu\text{g g}^{-1}$  for the legumes that have been grown in the mining areas [31]. The amount of Cd in the shoots of *A. effusus* and *A. microcephalus* was 0.4 and  $3.7 \text{ } \mu\text{g g}^{-1}$ , respectively (Figure 6). As a result, the ability of *A. microcephalus* in the absorbance and translocation of Cd was about 3.2 times more than that of *A. effusus* (16.7% versus 5.2%) (Figure 6). According to the literature, the soil pH is the major soil factor controlling the uptake of Cd [30]. Therefore, the information about pH of the soil samples could be useful in explaining the high ability of *A. microcephalus* in the absorbance of Cd compared to *A. effusus*.



**Figure 6.** The trend of trace element concentrations in the soils and shoot ashes of *A. microcephalus* from Agh-Dareh mine and *A. effusus* from Zarshouran mine.

The average U content in the Earth's crust was estimated to be  $2 \text{ } \mu\text{g g}^{-1}$ , and it has been reported that its content in uncontaminated soils varies in the order of  $1.9\text{--}4.4 \text{ } \mu\text{g g}^{-1}$ ; it is while the U content in the terrestrial plants was reported to be in the range of  $0.005\text{--}0.06 \text{ } \mu\text{g g}^{-1}$  [30]. The U concentration in the soils of the Zarshouran and Agh-Dareh mines ranges between  $2.4\text{--}4.7$  and  $1.4\text{--}2.1 \text{ } \mu\text{g g}^{-1}$ , respectively. These amounts were in the range of average U content in the Earth's crust. On the other hand, its amount in the plants shoots was  $0.1\text{--}0.3$  and  $0.5\text{--}1.3$  for *A. effusus* and *A. microcephalus*, respectively. It could be concluded that according to the reported worldwide ranges for the amount of U in the plants, the performance of these two species of *Astragalus*, especially *A. microcephalus*, in absorbance of U was considerable.

The average amounts of Tl have been reported to be about  $0.5$  and  $0.05 \text{ } \mu\text{g g}^{-1}$  in different soils and plants, respectively [30, 32]. These amounts for the soil of the Zarshouran mine and the shoots of

*A. effusus* grown in that mine were  $7.9$  and  $0.4 \text{ } \mu\text{g g}^{-1}$ , respectively. Moreover, in the Agh-Dareh mine, the mean content of Tl in the soil and shoot of *A. microcephalus* was determined to be  $32.8$  and  $7.7 \text{ } \mu\text{g g}^{-1}$ , respectively (Figure 5). By considering the average Tl content in the Earth's crust ( $0.5 \text{ } \mu\text{g g}^{-1}$ ), the content of the element in the soils of the Zarshouran and Agh-Dareh mines was high. Moreover, the Tl content in the plant ashes (especially in the case of *A. microcephalus*) was more than the worldwide reported averages of Tl in the plant samples.

Lead is one of the major chemical pollutants of the environment [33]. As the Pb concentration in the soils and vegetation has increased in the recent decades due to anthropogenic activities, being aware of its content in the soils and plants is very important in environmental sciences. The world average amount of the total Pb in Earth's crust and in different soils have been estimated to be  $15$  and  $27 \text{ } \mu\text{g g}^{-1}$ , respectively [30]. In contaminated sites such as mining areas, the Pb content is high. For



instance, its amount in non-ferrous metal mining areas may range from 15 to 13000  $\mu\text{g g}^{-1}$ , according to the literature [34, 35]. In the case of the Pb content in the plants, it has been reported that its amount in the legumes of different countries varies from 1 to 4  $\mu\text{g g}^{-1}$  at the plant immature growth, while other high amounts such as the range of 63-232  $\mu\text{g g}^{-1}$  have been reported for the plants grown in the contaminated sites (such as mining and mineralized areas) [36]. In the present study, the Pb mean amounts in the soils of the Zarshouran and Agh-Dareh mines were 282 and 1158  $\mu\text{g g}^{-1}$ , respectively. These amounts were approximately 19 and 80 times more than those of the Earth's crust, respectively. On the other hand, the Pb amounts in the shoots of *A. effusus* and *A. microcephalus* were 7.3 and 187  $\mu\text{g g}^{-1}$ , respectively (Figure 6). In fact, *A. microcephalus* absorbed about 16.1% of the soil's Pb content of the Agh-Dareh mine. The mentioned amount was 6.2 times more than that of *A. effusus* in lead absorbance and translocation from the soil of the Zarshouran mine (Figure 6). The Pb uptake by plants depends on some soil parameters such as the soil organic matter and pH. Moreover, some plant factors like genetic factors, root surface area, and root exudates are very important [30]. It has been reported that Pb is absorbed mainly by plant root hairs, and root surface area is a significant factor in Pb uptake by plants. Therefore, high potential of *A. microcephalus*, as a perennial plant, in Pb absorbance could be related to its advanced root system compared to *A. effusus*. However, the Pb content of plants grown in mineralized areas is highly correlated with Pb concentration in soils of such areas. Nevertheless, according to the literature, Pb is a very useful element for geochemical prospecting [37].

*A. effusus* in the Zarshouran mine exhibited a desirable performance in the absorbance and translocation of Cu, Mo, and Cr from the soil of the present area (Figures 5b and 6). The plant was absorbed, transferring about 45.6, 40.0, and 26.8 percent of the Cu, Mo, and Cr contents of the soil of the Zarshouran mine, respectively. In contrast, the absorbance and translocation ability of *A. microcephalus* for these elements was 25.9, 20.5, and 21 percent of the soil of the Agh-Dareh mine, respectively.

The abundance of Cu in the Earth's crust averages 55  $\mu\text{g g}^{-1}$  and its average content in different soil groups in the world ranges from 14 to 109  $\mu\text{g g}^{-1}$  [30]. The Cu content in the soil samples of the Zarshouran and Agh-Dareh mines was in the

range of 11-45 and 41-66  $\mu\text{g g}^{-1}$ , respectively. In agreement with the obtained mean amount of Cu in the shoots of the two examined *Astragalus* species (14 and 13.8  $\mu\text{g g}^{-1}$  for *A. effusus* and *A. microcephalus*, respectively), it has previously been reported that the Cu content of the whole plants shoots do not often exceed 20  $\mu\text{g g}^{-1}$  [30]. For instance, the mean level of Cu in the clovers (*Trifolium* sp., another member of the Fabaceae family) of different countries has been in the range of 6.5-16.2  $\mu\text{g g}^{-1}$  [30]. It is while some plant species can accumulate a high amount of this metal in their tissue and 24 Cu hyperaccumulating species have been recorded in various plant families [38] up to now. Cu is one of the essential metals in the plants, serving important roles in physiological processes such as photosynthesis and respiration, carbohydrate and nitrate metabolisms, disease resistance, and water permeability [39].

The Mo average content of the Earth's crust has been reported to be 1.5  $\mu\text{g g}^{-1}$ ; meanwhile, the world average amount of Mo in the soils has been established to be 0.9-1.8  $\mu\text{g g}^{-1}$ . The element is one of the essential micronutrients in the plants and plays an important role in the nitrogen metabolism and protein synthesis of the plants [40]. Various factors such as drought, soil pH and texture, and also plant species affect Mo phytoavailability [41]. According to the results of some previous studies, the mean Mo content in the legumes (Fabaceae family) ranges from 0.7 to 2.3  $\mu\text{g g}^{-1}$  in different countries, where the Mo toxicity in grazing animals has not been observed [30]. Therefore, the amount of Mo in the shoots of *A. effusus* (0.6  $\mu\text{g g}^{-1}$ ) and *A. microcephalus* (1.6  $\mu\text{g g}^{-1}$ ) was in the reported ranges for the Fabaceae family.

The average content of Cr in the Earth's crust and the world soils has been established to be 100 and 60  $\mu\text{g g}^{-1}$ , respectively. Due to the Cr importance as an essential micronutrient for the humans and its carcinogenic effects in high concentrations, the Cr content in the plants has recently received much attention [30]. Most soils contain high amounts of Cr but it is slightly available to plants and not easily translocate within them. It has been reported that the Cr concentration in the shoots of the Indian mustard and fodder radish growing in Cr-polluted soils (247  $\mu\text{g g}^{-1}$ ) does not exceed 10  $\mu\text{g g}^{-1}$  [42]. Moreover, the amounts of Cr in legumes and clover (both from Fabaceae) have been reported to be up to 0.5 and 4.2  $\mu\text{g g}^{-1}$ , respectively. The average obtained amount of Cr in the shoot ashes of *A. microcephalus* and *A.*

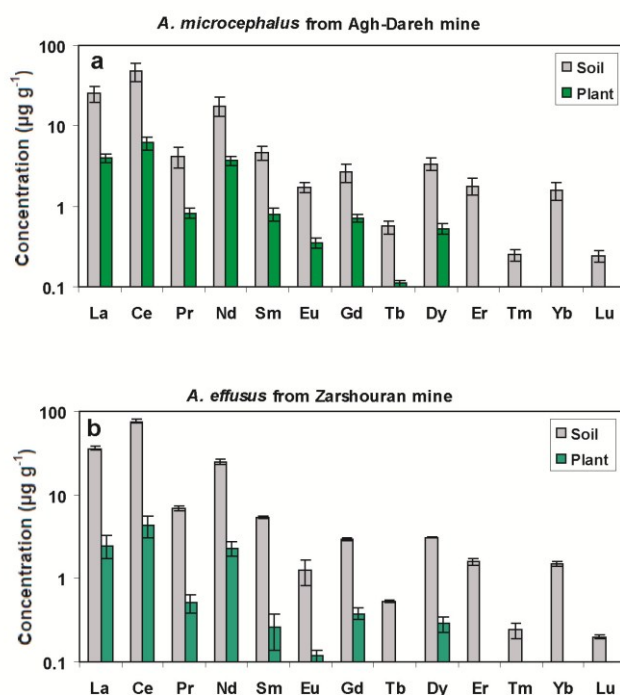
*effusus* was 24.2 and 15  $\mu\text{g g}^{-1}$ , respectively. Therefore, the potential of *A. effusus* in the absorbance and translocation of Cr was approximately more than that of *A. microcephalus*. In addition, the amount of Cr in the shoots of both examined plants was more than that for legumes and clover. It has been reported that the capability of the root of the plants in converting  $\text{Cr}^{3+}$  (slightly mobile) to  $\text{CrO}_4^{-2}$  (soluble) is the key process in Cr absorbance [30]. Therefore, good potential of the root of *A. effusus* in converting  $\text{Cr}^{3+}$  to  $\text{CrO}_4^{-2}$  and production of more soluble Cr content could be one of the main reasons of the high amount of Cr in that plant.

The average content of Cr in the soil samples of the Agh-dareh and Zarshouran mines was 114.4 and 56  $\mu\text{g g}^{-1}$ , respectively. Therefore, the content of Cr in the soil of the Agh-Dareh mine was more than that of the Earth's crust; it is while the element content in the soil samples of the

Zarshouran mine was lower than that of the Earth's crust.

### 3.3. Accumulation of rare elements

The rare earth elements (REEs) are usually related to the lanthanides (LAs) comprising a group of 15 elements, of which only promethium (Pm) does not exist naturally in the Earth's crust [30]. Due to the REEs economic importance and their high usage in different industries ranging from glass production to electronics industry, their different characteristics have been extensively studied. However, most of those studies have been focused on the geochemical characters of REEs on parent rocks and soils [43, 44], and there are few studies on their bio-geochemical and environmental behaviors in soil-plant systems. The REEs mean contents in the soil samples of the two studied mines and in the shoot ashes of *A. effusus* and *A. microcephalus* are presented in Figure 7.

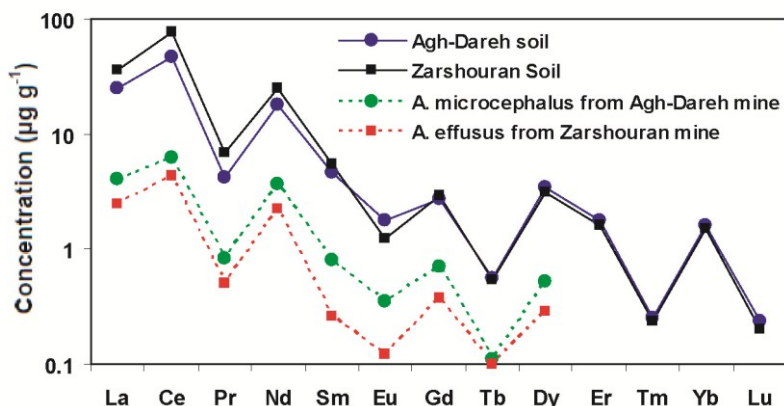


**Figure 7.** The amounts of rare earth elements in the soils and shoot ashes of a) *A. microcephalus* from Agh-Dareh mine and b) *A. effusus* from Zarshouran mine (Mean  $\pm$  SE).

REEs distribution shows a general peculiarity; their content is decreased with increase in the atomic weight; according to the Oddon-Harkins rule, an element with an even atomic number is more frequent than the next element with an odd atomic number [45]. Regarding the soils of the Zarshouran and Agh-Dareh mines, the amount of 13 analyzed REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb, and Lu) and their distribution

pattern approximately followed the mentioned rule (Figure 8). Moreover, the REE contents in the plants ashes (for La to Dy) were also in agreement with those estimated by the Oddon-Harkins rule (Figure 8); however, due to the very low amounts of Er, Tm, Yb, and Lu in the plant ash samples, and also due to the limitations associated with the analytical technique employed, their amounts were not determined (Figures 7 and 8).





**Figure 8.** The trend of rare earth element concentrations in the soils and shoot ashes of *A. microcephalus* from Agh-Dareh mine and *A. effusus* from Zarshouran mine.

According to the results obtained, the abundance of La, Ce, and Nd in the soils of the Zarshouran and Agh-Dareh mines was remarkable, and the content of light rare earth elements (LREEs, the elements from La to Gd) was higher than that of heavy rare earth elements (HREEs, the elements from Tb to Lu). During weathering processes, the REEs enrichment in the weathered material is relatively high, especially for LREEs [46]. The High amount of LREEs, in comparison to HREEs, has also been previously reported for the soil of the Hetai gold field in China [47]. The ratios of the sum concentration of LREEs to HREEs ( $\sum \text{LREE}/\text{HREE}$ ) for the soils of the Zarshouran and Agh-Dareh mines were 21.4 and 13.2, respectively. HREEs are more likely to move than LREEs. Thus during the migration process of REEs, LREEs could be enriched in parent rocks, while HREEs might be gradually depleted. Therefore, the  $\sum \text{LREE}/\text{HREE}$  ratio could reflect the hot and humid weathering conditions and the low-pH leaching environment in the mineralization area [47]. The total concentration of REEs except Ho ( $\sum \text{REEs}$ , the sum of the concentration of REEs except Ho) in the soils of the Zarshouran and Agh-Dareh mines was 160.8 and 111.6, respectively.

The process of REEs absorbance, accumulation, and transportation in a plant system is influenced by the soil chemical properties and bio-availability of REEs, and plant survival mechanisms in the mining area [48]. Laul et al. have determined the REEs relative abundance, finding that the concentration of these elements in plants followed their occurrence in the soil [49]. The existence of a significant similarity or correlation between the REEs contents of the soils of the two studied mines and the plants of each mine was in agreement with the findings of the

previous research works. In fact, the amount of each REE was increased in the plant by its enhancement in the soil of the related mine (Figure 8). According to the results obtained, both plant species absorbed and transported much more LREEs than HREEs. The high ability of some plant species such as *Dicranopteris dichotoma* in the absorbance of more LREEs than HREEs has been reported previously [47]. Plants by their root exudates such as organic acids can solubilize LREEs in the soil; moreover, there are many carboxylate groups in plant tissues, which can bind to LREEs more easily and more effectively than HREEs. The  $\sum \text{LREEs}$  contents in the plants shoot ashes were 10.3 and 16.6  $\mu\text{g g}^{-1}$  of *A. effusus* and *A. microcephalus*, respectively. Meanwhile, due to the very low amounts of 4 numbers of HREEs (Er, Tm, Yb, and Lu), their contents and also  $\sum \text{HREEs}$  could not be determined. The performance of *A. microcephalus* in the Agh-Dareh mine regarding the uptake and transportation of REEs was more than that of *A. effusus* in the Zarshouran mine. Some REEs such as Nd, Eu, and Gd were absorbed up to more than 20% of their soil contents by *A. microcephalus*; thus it could be concluded that *A. microcephalus* was more capable than *A. effusus* in the uptake of REEs.

### 3.4. Biological absorption potential

The chemical analysis of plants can be a promising tool to determine the properties of the biosphere. The biological absorption coefficient (BAC) reflects the relationship between the concentration of chemical elements in the soil and in the plant; moreover, it could be used for comparing different plants abilities in the absorption of the elements [50]. The bio-accumulation amount of each element by

plants was classified into five groups according to the quantity of BAC:  $BAC > 10$ , very strong accumulation; from 1 to 10, strong accumulation; from 0.1 to 1.0, moderate absorption; from 0.01 to 0.1, weak absorption; and from 0.001 to 0.01, very weak absorption [51].

As it can be seen in Figure 9a, the average amount of BAC for P, S, K, Ca, and Zn (in the major element group) was more than 1, and in some cases (P and S for *A. effusus*), it was more than 10 for the two examined plant species. In fact, these elements could be strongly accumulated in the studied plants. The potential of *A. effusus* in the biological absorption of the mentioned elements was 5.7, 10.1, 2.4, 2.1, and 3 times more than that of *A. microcephalus*, respectively. Moreover, according to the amounts of BAC, the performance of *A. effusus* in the absorption of Mg, Fe, and Mn was remarkably more than that of *A. microcephalus* (Figure 9a). In contrast, BACs of Al and Ti for *A. microcephalus* were 0.31 and 0.42, respectively, and these amounts were significantly more than their BAC values for *A. effusus* (0.04 and 0.01, respectively).

All BAC values for the 11 elements that were studied as trace elements in the soils of the Zarshouran and Agh-Dareh mines were in the range of 0.1-1 (Figure 9b). However, BAC values of Cu and Cr for *A. effusus* from that of

Zarshouran mine were much higher than those for *A. microcephalus*. In addition, the potential of *A. microcephalus* in the absorbance of Cd, U, and Ti was more than that of *A. effusus* according to the BAC values of these elements in the two plant species (Figure 9b).

According to the amounts obtained, as found for BAC values of REEs, the potential of *A. microcephalus* in the absorption and translocation of REEs was considerable in comparison with that of *A. effusus*. BAC values of REEs, especially LREEs, for *A. microcephalus* were noticeably higher than those of *A. effusus* (Figure 9c). For instance, the BAC values of *A. microcephalus* for Ce, Pr, Nd, and Gd were 0.74, 5.2, 2.4, and 1.4 respectively. Meanwhile, these amounts for *A. effusus* were 0.05, 0.07, 0.09, and 0.13, respectively. Therefore, contrary to the results obtained, while a good performance of *A. effusus* in the absorbance of major elements was found, its potential in the absorbance of REEs was very low.

Different potentials of the plants in the absorbance of the elements could be due to different reasons such as the abundance of the elements in the soil, pH and soil organic matter, bio-availability of the elements, plant age, and depth of root system [7, 52].

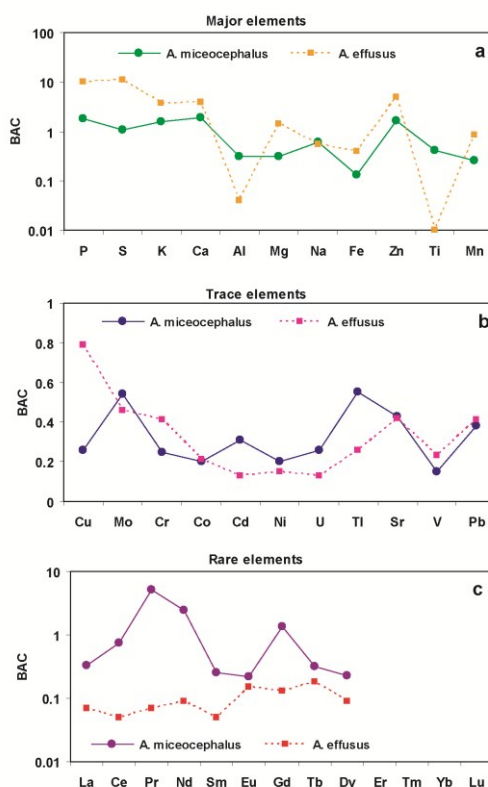


Figure 9. Comparing BAC mean values of a) major, b) trace, and c) rare earth elements for the sampled plants in the studied areas.

#### 4. Conclusions

In the present study, the environmental bio-geochemical characteristics of some major, trace, and rare earth elements were investigated in two main gold deposits of Iran, and the bio-accumulation potentials of two *Astragalus* species for their uptake were probed. According to the results obtained, regarding the accumulation of the elements in the soil samples and the shoot ashes of the plants, among the 11 elements studied as the major elements (P, S, K, Ca, Al, Mg, Na, Fe, Zn, Ti, and Mn), *A. effusus* in the Zarshouran mine passed a high ability in the accumulation of the some major elements such as S, P, K, Ca, and Zn. In contrast, only P was accumulated in the shoot of *A. microcephalus* more than the soil samples in the Agh-Dareh mine. In the case of the trace elements, although the amounts of the examined trace elements in the soil samples were more than those in the shoots of both examined plants, the potential of *A. microcephalus* in the absorbance and translocation of Cd, U, Tl, and Pb from the soil of Agh-Dareh was more than that of *A. effusus*. *A. effusus* also showed a good performance in the absorbance of Cu and Cr in comparison with *A. microcephalus*; also BAC values of Cu and Cr for *A. effusus* from the Zarshouran mine were much higher than those for *A. microcephalus*. In addition, the performance of *A. microcephalus* in the Agh-Dareh mine regarding the uptake and transportation of REEs was more than that of *A. effusus* in the Zarshouran mine. BAC values of REEs, especially LREEs, for *A. microcephalus* were noticeably higher than those of *A. effusus*. Both plant species absorbed and transported much more light REEs rather than heavy ones. It could be concluded that the performance of *A. effusus* in the absorbance of major elements was considerable. In contrast, *A. microcephalus* showed a good performance in the uptake of the trace and rear earth elements from the soil of Agh-Dareh mine.

#### Acknowledgments

The authors wish to thank the Urmia University for providing all kinds of supports during the present study.

#### References

[1]. Ansari, A.A., Gill, S.S., Gill, R., Lanza, G.R. and Newman, L. (2015). Phytoremediation: Management of environmental contaminants, Springer International Publishing, Switzerland.

[2]. Liang, H.M., Lin, T.H., Chiou, J.M. and Yeh, K.C. (2009). Model evaluation of the phytoextraction

potential of heavy metal hyperaccumulators and non-hyperaccumulators. Environ. Pollut. 157: 1945-1952.

[3]. Sasmaz, M. and Sasmaz, A. (2017). The accumulation of strontium by native plants grown on Gumuskoy mining soils. J. Geochem. Explor. 181: 236-242.

[4]. Sasmaz, M., Akgül, B., Yıldırım, D. and Sasmaz, A. (2016). Mercury uptake and phytotoxicity in terrestrial plants grown naturally in the Gumuskoy (Kutahya) mining area, Turkey. Int. J. Phytoremediation. 18: 69-76.

[5]. Robinson, B.H., Anderson, C.W.N. and Dickinson, N.M. (2015). Phytoextraction: Where's the action? J. Geochem. Explor. 151: 34-40.

[6]. Krämer, U. (2010). Metal hyperaccumulation in plants. Annu. Rev. PLant Biol. 61: 517-534.

[7]. Sheoran, V., Sheoran, A.S. and Poonia, P. (2016). Factors affecting phytoextraction: a review. Phedosphere. 26: 148-166.

[8]. Baker, A.J.M. (1981). Accumulators and excluders -strategies in the response of plants to heavy metals. J. Plant Nutr. 3: 643-654.

[9]. Baker, A.J.M., McGrath, S.P., Reeves, R.D. and Smith, J.A.C. (2000). Metal hyperaccumulator plants: a review of the ecology and physiology of a biological resource for phytoremediation of metal-polluted soils, In *Phytoremediation of contaminated soil and water*; Terry, N. and Bañuelos, G. Eds.; Lewis Publishers: Boca Raton. pp. 85-107.

[10]. Baker, A.J.M. and Brooks, R.R. (1989). Terrestrial higher plants which hyperaccumulate metallic elements: a review of their distribution, ecology and phytochemistry. Biorecovery. 1: 81-126.

[11]. Adriano, D.C. (2001). Trace elements in terrestrial environment: biogeochemistry, bioavailability and risks of metals, 2<sup>ed</sup>., Springer-Verlag, New York.

[12]. Ghaderian, S.M. and Ghotbi Ravandi, A.A. (2012). Accumulation of copper and other heavy metals by plants growing on Sarcheshmeh copper mining area, Iran. J. Geochem. Explor. 123: 25-32.

[13]. Lasat, M.M. (2002). Phytoextraction of toxic metals. J. Environ. Qual. 31: 109-120.

[14]. Daliran, F. (2008). The carbonate rock-hosted epithermal gold deposit of Agdarreh, Takab geothermal field, NW Iran- hydrothermal alteration and mineralisation. Miner. Deposita. 43: 383-404.

[15]. Asadi, H.H., Voncken, J.H.L., Kühnel, R.A. and Hale, M. (2000). Petrography, mineralogy and geochemistry of the Zarshuran Carlin-like gold deposit, northwest Iran. Miner. Deposita. 35: 656-671.

[16]. Mehrabi, B., Yardley, B.W.D. and Cann, J.R. (1999). Sediment-hosted disseminated gold

mineralisation at Zarshuran, NW Iran. Miner. Deposita. 34: 673-696.

[17]. Modabberi, S. and Moore, F. (2004). Environmental geochemistry of Zarshuran Au-As deposit, NW Iran. Environ. Geol. 46: 796-807.

[18]. Shahmoradi, S., Afyuni, M. and Hajabbasi, M.A. (2017). Speciation, fractionation and plant availability of arsenic as induced by sorbents mixed with soil of Zarshuran (Iran). Int. J. Environ. Sci. Technol. 14: 767-776.

[19]. Jalili, A. and Jamzad, Z. (1999). Red data book of Iran: a preliminary survey of endemic, rare and endangered plant species of Iran Research Institute of Forests and Rangelands, Tehran.

[20]. Movafeghi, A., Naghiloo, S. and Dadpour, M.R. (2011). Inflorescence and floral development in *Astragalus lagopoides* Lam. (Leguminosae: Papilionoideae: Galegeae). Flora- Morphology, Distribution, Functional Ecology of Plants. 206: 219-226.

[21]. Podlech, D. (2008). The genus *Astragalus* L. (Fabaceae) in Europe with exclusion of the former Soviet Union. Feddes Repert. 119: 310-387.

[22]. Ghaderian, S.M. and Baker, A.J.M. (2007). Geobotanical and biogeochemical reconnaissance of the ultramafics of Central Iran. J. Geochem. Explor. 92: 34-42.

[23]. Alavi, M. (1994). Tectonics of the zagros orogenic belt of iran: new data and interpretations. Tectonophysics. 229: 211-238.

[24]. Karimi, N., Ghaderian, S.M., Maroofi, H. and Schat, H. (2009). Analysis of arsenic in soil and vegetation of a contaminated area in Zarshuran, Iran. Int. J. Phytoremediation. 12: 159-173.

[25]. Kovalevsky, A.L. (1995). Barrier-free biogeochemical prospecting, In *Biological systems in mineral exploration and processing*; Brooks, R.R., Dunn, C.E. and Hall, G.E.M. Eds.; Ellis Horwood: London. pp. 283-300.

[26]. Schachtman, D.P., Reid, R.J. and Ayling, S.M. (1998). Phosphorus uptake by plants: from soil to cell. Plant Physiol. 116: 447-453.

[27]. Leustek, T. and Saito, K. (1999). Sulfate transport and assimilation in plants. Plant Physiol. 120: 637-644.

[28]. White, B.J. and Broadley, M.R. (2003). Calcium in plants. Ann. Bot-London. 92: 487-511.

[29]. Maathuis, F.J.M. and Sanders, D. (1996). Mechanisms of potassium absorption by higher plant roots. Physiol. Plantarum. 96: 158-168.

[30]. Kabata-Pendias, A. (2010). Trace Elements in Soils and Plants, Fourth ed., CRC Press, Florida.

[31]. Mathews, H. and Thornton, I. (1980). Agricultural implication of Zn and Cd contaminated

land at Shipham, Somerset, In *Trace Substances in Environmental Health*; Hemphill, D.D. Ed. University of Missouri: Missouri, Columbia. 478 P.

[32]. Markert, B. (1992). Multi-element analysis in plants material: analytical tools and biological questions, In *Biogeochemistry of Trace Elements*; Adriano, D.C. Ed. CRC Press: Boca Raton, Florida. 401 P.

[33]. Mohtadi, A., Ghaderian, S.M. and Schat, H. (2012). Lead, zinc and cadmium accumulation from two metalliferous soils with contrasting calcium contents in heavy metal-hyperaccumulating and non-hyperaccumulating metallophytes: a comparative study. Plant Soil. 361: 109-118.

[34]. Huff, L.C. (1976). Migration of lead during oxidation and weathering of lead deposits., In *Lead in the Environment. Geological Survey Professional Paper* Lovering, T.G. Ed. United States Government Printing Office: Washington. pp. 21-40.

[35]. Ferreira da Silva, E., Zhang, C., Serrano Pinto, L.S., Patinha, C. and Reis, P. (2004). Hazard assessment on arsenic and lead in soils of Castromil gold mining area, Portugal. Appl. Geochem. 19: 887-898.

[36]. Roberts, T.M., Gizyn, W. and Hutchinson, T.C. (1974). Lead contamination of air, soil, vegetation and people in the vicinity of secondary lead smelters, In *Trace Substances in Environmental Health*; Hemphill, D.D. Ed. University of Missouri: Columbia, MO. pp. 155.

[37]. Nriagu, J.O. (1978). The biogeochemistry of lead in the environment, Elsevier/North-Holland Biomedical Press, Amsterdam.

[38]. McGrath, S.P. (1998). Phytoextraction for soil remediation, In *Plants that Hyperaccumulate Heavy Metals*; Brooks, R.R. Ed. CAB Intern: Wallingford, UK. pp. 261-385.

[39]. Yruela, I. (2005). Copper in plants. Braz. J. Plant. Physiol. 17: 145-156.

[40]. Alam, F., Kim, T.Y., Kim, S.Y., Alam, S.S., Pramanik, P., Kim, P.J. and Lee, Y.B. (2015). Effect of molybdenum on nodulation, plant yield and nitrogen uptake in hairy vetch (*Vicia villosa* Roth). Soil Sci. Plant Nutr. 61: 664-675.

[41]. Zakikhani, H., Khanif, Y.M., Anuar, A.R., Radziah, O. and Soltangheisi, A. (2014). Effects of different levels of molybdenum on uptake of nutrients in rice cultivars. Asian J. Crop Sci. 6: 236-244.

[42]. Simon, L., Prokisch, J., Kovács, B. and Gy'ori, Z. (1998). Phytoextraction of heavy metals from a galvanic mud contaminated soil, In *Soil Pollution*; Filep, G. Ed. Agricultural University of Debrecen: Debrecen, Hungary. pp. 289-295.

- [43]. Mao, G., Hua, R., Gao, J., Li, W., Zhao, K., Long, G. and Lu, H. (2009). Existing forms of REE in gold-bearing pyrite of the Jinshan gold deposit, Jiangxi Province, China. *J. Rare Earth*. 27: 1079-1087.
- [44]. Abedini, A. and Calagari, A.A. (2017). REEs geochemical characteristics of lower Cambrian phosphatic rocks in the Gorgan-Rasht Zone, northern Iran: Implications for diagenetic effects and depositional conditions. *J. Afr. Earth Sci.* 135: 115-124.
- [45]. Markert, B. (1987). The pattern of distribution of lanthanide elements in soils and plants. *Phytochemistry*. 26: 3167-3170.
- [46]. Duddy, L.R. (1980). Redistribution and fractionation of rare-earth and other elements in a weathering profile. *Cem. Geol.* 30: 363-381.
- [47]. Miao, L., Ma, Y., Xu, R. and Yan, W. (2011). Environmental biogeochemical characteristics of rare earth elements in soil and soil-grown plants of the Hetai goldfield, Guangdong Province, China. *Environ. Earth Sci.* 63: 501-511.
- [48]. Tyler, G. (2004). Rare earth elements in soil and plant systems: a review. *Plant Soil*. 267: 191-206.
- [49]. Laul, J.C., Weimer, W.C. and Rancitelli, L.A. (1979). Biogeochemical distribution of rare earths and other trace elements in plants and soils, In *Origin and Distribution of the Elements*; Ahrens, L.H. Ed. Pergamon Press: Oxford, pp. 819-827.
- [50]. Imbernon, R.A.L. and Rocha, R.G. (2016). Biogeochemical coefficients as indicators of nutrient element sorption in jerivá (*Syagrus romanzoffiana* (Chamisso) Glassman), a palm tree species from Brazil. *Environ. Earth Sci.* 75 (6): 515.
- [51]. Perel'man, A.I. (1966). Landscape geochemistry (translation no. 676, Geological Survey of Canada, 1972), Vysshaya Shkola, Moscow.
- [52]. Maria do Carmo, L.I.M.A., Nardi, L.V.S., Pereira, V.P., NETO, A.C.B. and Vedana, L.A. (2014). Evaluation of biological absorption coefficient of trace elements in plants from the pitinga mine district, amazonian region. *Revista do Instituto Geológico, São Paulo*. 35 (1): 19-29.

## تجمع زیستی عناصر اصلی، جزئی و نادر خاکی توسط دو گونه گون رشد یافته در کانسار طلای آق دره و زرشوران، تکاب، شمال غرب ایران

سمانه تربیتی<sup>۱\*</sup>، صمد علیپور<sup>۲</sup>، معصومه رستمی<sup>۲</sup> و صابر حاجی علیزاده<sup>۲</sup>

۱- گروه علوم محیط زیست، پژوهشکده مطالعات دریاچه ارومیه، دانشگاه ارومیه، ایران

۲- گروه زمین شناسی، دانشکده علوم، دانشگاه ارومیه، ایران

ارسال ۲۰۱۸/۴/۲۱، پذیرش ۲۰۱۸/۵/۳۰

\* نویسنده مسئول مکاتبات: s.torbati@urmia.ac.ir

### چکیده:

معادن طلای آق دره و زرشوران دو کانسار طلای فعال در تکاب، شمال غرب ایران می باشند. در پژوهش حاضر، توانایی دو گونه گون (*Astragalus*) *A. microcephalus* از معدن آق دره و *A. effusus* از معدن طلای زرشوران) به عنوان گیاهان غالب رشد یافته، در این مناطق از نظر تجمع زیستی عناصر اصلی، جزئی و نادر خاکی ارزیابی شدند. نمونه های گیاهی و خاکی از محدوده ی معادن مذکور جمع آوری و توسط طیف سنجی جرمی پلاسمای جفت شده القائی (ICP-MS) مورد آنالیز واقع شدند. مطابق نتایج به دست آمده، *A. effusus* از معدن زرشوران دارای توانایی بالایی در تجمع برخی عناصر اصلی مانند S، P، K، Ca و Zn است. اگرچه مقادیر عناصر جزئی مورد مطالعه در نمونه های خاک بیشتر از مقادیر موجود در نمونه های خاکستر اندام هوایی دو گونه مورد مطالعه بود، با این حال توانایی *A. microcephalus* در جذب و انتقال Cd، U، Tl و Pb بیشتر از توانایی *A. effusus* تعیین شد. مشخص شد که کارایی *A. microcephalus* از معدن آق دره در جذب و انتقال عناصر نادر خاکی (REEs) بیشتر از *A. effusus* از معدن زرشوران است. اگرچه هر دو گونه ی گیاهی مقادیر بیشتری از عناصر نادر خاکی سبک را نسبت به انواع سنگین جذب کرده و منتقل می کنند. مطابق نتایج به دست آمده، پژوهش حاضر برخی یافته ژئوشیمیائی را در مورد بستر ارائه می دهد و منجر به افزایش اطلاعاتی در مورد گیاهان، به عنوان شاخص مفید برای کانی سازی فلزات می شود.

**کلمات کلیدی:** گون، تجمع زیستی، کانسار طلا، آق دره، زرشوران.