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# Phytoremediation Potential of Native Hyperaccumulator Plants Growing on Heavy Metal-Contaminated Soil of Khatunabad Copper Smelter and Refinery, Iran

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**Citation:** Siyar, R.; Doulati Ardejani, F.; Norouzi, P.; Maghsoudy, S.; Yavarzadeh, M.; Taherdangkoo, R.; Butscher, C. Phytoremediation Potential of Native Hyperaccumulator Plants Growing on Heavy Metal-Contaminated Soil of Khatunabad Copper Smelter and Refinery, Iran. *Water* **2022**, *14*, 3597. https://doi.org/10.3390/w14223597

Academic Editors: Patrizia Brunetti and Giuseppe Capobianco

Received: 11 October 2022
Accepted: 4 November 2022
Published: 8 November 2022



**Abstract:** The characterization of prospective plants is one of the critical issues in the efficiency and success of the phytoremediation process. Due to adaption and tolerance to different environmental stresses, native plant species have priority in this method. This study examined fifty plants of five species, namely *Launaea acanthodes*, *Artemisia* sp., *Cousinia congesta*, *Peganum harmala*, and *Stipa* sp., growing near a smelter and refinery in Iran to identify potential species for phytoextraction and phytostabilization. Therefore, Pb, Ni, Mn, Mo, S, and Cu concentrations in sampled plants and soils were analyzed. Three different pollution indices, namely metal accumulation index (MAI), translocation factor (TF), and bioconcentration factor (BCF) were used for evaluating the metal concentrations in roots and shoots of each plant species. The results indicated that *Artemisia* sp., with values of 3.21, 1.09, and 1.14 for MAI, BCF, and TF, respectively, is appropriate for phytoextraction in the study area. Plants such as *Launaea acanthodes* and *Cousinia congesta* with high BCF and low TF values showed the potential for phytostabilization. Investigating the indices for different elements demonstrated that *Launaea acanthodes* had a BCF value greater than 1 and a TF value less than 1; therefore, this plant could be used in the phytoremediation of arsenic through the phytostabilization technique. Furthermore, copper has very low bioavailability in these plant species. In addition, these native plant species were highly capable of accumulating sulfur from the soil because the BCF and TF indices for all inspected species were higher than 1; for *Launaea acanthodes*, the relevant TF value was about 10. The proposed native plant could be applied in practical applications of phytoremediation for soil remediation of contaminated sites around the metal factories and mines in southeastern Iran.

**Keywords:** *Artemisia* sp.; MAI; phytoextraction; phytostabilization; principal component analysis

## 1. Introduction

Mining is one of the main industries that play an important role in the economic development of countries. However, mining activities and the release of toxic elements adversely affect soil and water quality and pose a serious threat to human health and natural ecosystems [1]. In the last few decades, pollution by heavy metals has become a demanding environmental concern because of the bioaccumulation of heavy metals in the food chain. The rising level of heavy metals in the environment is the consequence of natural processes and human activities such as rock weathering, soil erosion, volcanic eruptions, industrial emissions, urban runoff, metallurgical processes, mining activities, industrial effluents, insecticides, and fertilizers [2].

There are several technologies, such as soil replacement, surface capping, vitrification, and immobilization, which can be applied to remediate soil contaminated by heavy metals. However, many of these technologies are expensive or do not offer long-term solutions [3]. In addition, some other remediation methods can have adverse effects on the structure, fertility, and biological activity of the soil [4]. Phytoremediation technology is associated with risks due to the accumulation of trace elements in plant organs and reduced plant growth in the presence of these elements in the soil due to toxicity. Consequently, the efficiency of plants in removing heavy metals from the soil is reduced. Nevertheless, this technique has been widely used due to its high rate of heavy metal uptake, lower cost compared to traditional methods, soil structure preservation, and minimum adverse environmental impacts [5].

Phytoremediation is an operative and efficient method for removing different types of contaminants from soil [6]. Phytoremediation is a plant-based technology in which natural plants are used to remediate contaminated sites. In other words, phytoremediation uses a plant as a soil amendment to decrease hazardous pollutants. There are two strategies involved in phytoremediation. The first strategy is phytostabilization in which resistant plants are used to stabilize heavy metals. Phytostabilization involves reducing heavy metals' mobility, toxicity, and bioavailability in the soil. With the use of this technology, the pollutants are reduced from the site without being removed directly. Phytostabilization aims to hinder the movement of metal contaminants, hence not allowing them to enter the water cycle and food chain.

Phytoextraction is the other strategy; it involves the uptake of heavy metals from the soil [7]. Phytoextraction is the ability of plant organs to remove toxic elements from the soil with the adsorption process. The contaminated plants can be harvested to remove or extract toxic elements.

Phytoextraction is based on absorbing the metals from the soil by plant roots in which different types of hyperaccumulator plants are substantially involved [8]. The ability of plant roots to absorb contaminants from the soil is the critical point in phytoextraction process. Phytoremediation techniques or techniques of applying hyperaccumulators in contaminant remediation have raised some concerns. Environmentalists believe that some plant species used for phytoremediation can invade the surrounding natural areas, thus disrupting and altering ecosystem functions, reducing native biodiversity, and adversely affecting the local economy and human health [9]. They may change the nature of ecosystem function as well. Therefore, in the new insight into phytoremediation, scientists try to use wild and cultivated plants as hyperaccumulators [10].

Native plants are easy to plant, and they are more compatible with the climatic conditions of the area and can resist different kinds of environmental stresses in the area compared to alien plants [11]. Therefore, indigenous wild plants are the most useful solution in the phytoremediation of heavy metals [12]. In the phytoremediation process, it is a great benefit to investigate the study area and find some native plants for extracting or stabilizing heavy metals in degraded and contaminated soils [13].

Phytoremediation of heavy-metal-contaminated soils is necessary for the diminution of environmental risks. Research on the use of plants to clean contaminated sites has a long history [4,6,10–12]. However, only a few studies have examined the potential of phytoremediation through native (indigenous) plants under certain conditions [14–16]. In other words, the use of native plants in cleaning soils contaminated with heavy metals having both of geogenic or anthropogenic origin in copper smelters and refineries has not been well addressed.

Phytoremediation innovations are available for various environments and types of contaminants [17–31]. However, the innovation of the present paper was the screening of native plant species for their potential and suitability for remediation of the study area. Laghlimi et al. [32] reviewed the mechanisms of phytoremediation of soils contaminated by heavy metals. They discussed the main factors influencing heavy metal uptake by plant species. These authors addressed different procedures for the phytoremediation of heavy-metal-contaminated soils. Nadgórska-Socha et al. [33] investigated the distribution of elements in three pseudo-metallophyte species (*Cardaminopsis arenosa*, *Plantago lanceolata*, and *Plantago major*) at metalliferous and non-metalliferous sites in southern Poland. They measured the accumulation of elements in shoots and roots of the plants. The authors found that the amount of the accumulated trace elements was higher in *Cardaminopsis arenosa* and *Plantago lanceolata* from metalliferous sites. The study further showed that the greatest amounts of Cd, Zn, Pb, Al, Fe, and Mn were in *Cardaminopsis arenosa*. Due to higher translocation coefficients (TF> 1) for zinc and cadmium in *Cardaminopsis arenosa* shoots, this species can be suitable for phytoextraction from soil.

In a study, Bozdogan Sert et al. [34] investigated heavy metal accumulation in the rosemary leaves and stems (as biomonitors) exposed to pollution resulting from traffic.

The results revealed that the rosemary had a reasonable capacity to accumulate heavy metals, including Al, Cd, Cr, Cu, Fe, Mn, Pb, and Zn, in both leaves and stems. They concluded that rosemary could be a good indicator for determining the amount of traffic-related pollution in urban areas.

Sevik et al. [35] determined the variation of heavy metal accumulation in some landscape plants grown in the city center of Kastamonu subject to plant type, plant organism, washing status, and traffic density. They collected leaf and branch samples of Ligustrum vulgare L., Euonymus japonica Thunb., Biota orientalis L., Juniperus sabina L., Berberis thunbergii DC, Mahonia aquifolium (Pursh) Nutt., and Buxus sempervirens L. plant species and analyzed them for some heavy metals, including lead. The results showed that Pb concentration was higher in branches relative to the leaves for all the species.

In a review paper, Siyar et al. [36] examined the pollutants produced in copper metallurgical factories. They briefly compared the different remediation methods used to reduce the environmental pollution related to these factories.

Siyar et al. [37] investigated the potential of vetiver in the phytoremediation process of soil contaminated with toxic metals around a metal smelter. In this study, the electrokinetic process was also applied to increase the removal efficiency of metals from contaminated soil. The results showed that vetiver has electro-phytoremediation potential for metal-contaminated soils. The vetiver grass accumulated 11,727 ppm of different elements. The results further showed that electrokinetic-assisted phytoremediation by applying AC current facilitated the translocation of the toxic metals from the soil to the plant shoots.

Sevik et al. [38] used the tree rings of cedar trees (*Cedrus* sp.) as biomonitors to monitor heavy metal accumulation in the atmosphere in urban areas. They determined the element concentrations in the inner and outer bark. It was found that the heavy metal concentrations in the outer bark were higher than those in the inner part.

Cetin et al. [39] evaluated the concentrations of Ca, Cu, and Li elements in the washed and unwashed needles, branches, and barks of blue spruce (*Picea pungens*) to calculate the recent concentration of heavy metals. The results showed that the concentration of the heavy metals changed dependent on the organ, washing status, and organ age. Overall, the lowest concentrations of Ca and Cu elements were obtained in the barks.

Alaqouri et al. [40] investigated the possibility of using Scots pine needles as biomonitor to determine heavy metal accumulation. The samples were collected in 1 km, 3 km, 10 km, and 25 km distances around a processing plant and magnesite mine in Russia. The results showed that the concentrations of heavy metals changed with the distance from the plant and needle age.

Sevik et al. [41] determined the changes in Ni, Co, and Mn concentrations in the leaves, branches, barks, and fruits of some trees, including cherry, plum, mulberry, and apple, growing in areas with dense traffic, low-density traffic, and no traffic in Kastamonu province of Turkey. The results showed an increase in the concentrations of Ni and Co elements in many organs as a function of traffic density.

Rosatto et al. [42] studied the response of roots and shoots to Ni in hyperaccumulator and non-hyperaccumulator plant species. They focused the study on the species *Alyssoides utriculata* (L.) Medik. and *Noccaea caerulescens* (J. Presl and C. Presl) F.K. Mey. as Ni hyperaccumulators and on the species *Alyssum montanum* L. and *Thlaspi arvense* L. as Ni non-hyperaccumulators. Based on their findings, hyperaccumulators did not display a Ni-dependent decline in root surfaces and biomass.

Cesur et al. [43] studied the capability of *Cupressus arizonica* annual rings to monitor the variations in heavy metal concentration in the atmosphere. In fact, they used trees as biomonitors in determining the increase in heavy metal concentrations in the air. The concentrations of Bi, Cd, and Ni in the outer bark, inner bark, and wood were compared in the inward-facing and road-facing parts. In addition, the variations in heavy metal concentrations in the annual rings were evaluated on a yearly basis. The results showed that the concentrations of elements in the outer bark of the road-facing part were at a higher level.

Cetin and Jawed [44] investigated the accumulation of Ba concentrations in some plants grown in Pakistan. Changes in Ba concentration in leaves and branches of *Ficus bengalensis*, *Ziziphus mauritiana*, *Conocarpus erectus*, and *Azadrechta indica* species depending on traffic density were determined. They found that the most suitable species for Ba concentration monitoring was *Azadrechta indica*, and the most suitable organs were *Azadrechta indica* leaves.

Heavy metals in soil are found in various solid-phase fractions. They can be subdivided into the following forms: easily soluble, water soluble, exchangeable, carbonate-bound, oxide-bound, Fe and Mn oxides, organically bound, silicate-bound, and residual [45]. The part of the soil that is easily soluble in the water is critical in environmental studies due to having the highest mobility, availability, and toxicity. Therefore, it is highly important in the environment and plays a vital role in diverse environmental issues [46]. From an ecological point of view, the soluble fraction of nutrients and toxicants in soils is significant. Plants can absorb the soluble fraction, and on the other hand, the soluble fraction part of the soil can leach into groundwater and cause environmental concerns [47].

There are two mechanisms by which plants can absorb heavy metals from the soil. One of them is the absorption of the soluble component in the soil solution, and the other is solubilization by root exudates [48]. While the current research takes into account the performance of phytoremediation and the heavy metal uptake of native plant species in the Khatunabad plain, the main focus is on soluble forms of the HMs. A high proportion of the total metal concentration in soils is in the insoluble fraction. This fraction is not immediately bioavailable for the plants and therefore is not directly toxic.

Another critical point is that microorganisms in the soil can absorb heavy metals in soluble and insoluble forms [49]. In the current study, sequential extraction has an essential role in evaluating the concentration of trace elements in soils and plants before and after absorption. The sequential extraction technique can assess the bioavailability of metals and their mobility in the soil [50]. Afterward, their potential hazard and toxicity in the environment can be predicted.

In this current study, the capability of heavy metal accumulation of five native plant species was investigated around the Khatunabad copper smelter and refinery (KHCSR) to discover hyperaccumulator plants in the region. The smelter has caused numerous environmental pollutions in the surrounding soils due to non-compliance with environmental standards. Since the contaminated area is very wide, phytoremediation is one of the main proposed methods to remediate the area and prevent the further spread of contamination.

Although in the research conducted by Einollahi and Pakzad [51] in the study area, the concentration of copper in the plant species *Lactuca serriola*, *Artemisia sieberi*, and *Astragalus bisulcatus* was investigated, these authors only measured the concentration of copper. In the present study, we selected five representative and indicator plant species and investigated their capability to remove a number of toxic heavy metal pollutants around the Khatunabad copper smelter and refinery.

In the past, many studies have been conducted regarding the use of phytoremediation in removing pollutants from water and soil environments. In these studies, metal removal processes such as phytostabilization and phytoextraction by various plant species have been evaluated, and based on these studies, plant species appropriate to the climate and growth conditions of each region have been introduced for phytoremediation of areas affected by various pollutants. Although the current research is inspired by the previous methodology, the important message of this article is the introduction of natural plant species that were able to successfully remove the environmental pollutants produced in the soil system in a site affected by a mining-related industry. In addition, the mechanisms by which each plant species reduces metal pollutants were determined with low cost and only by using some pollution indices in the study area.

The present study investigates the accumulation of As, Cu, Mo, Mn, Ni, Pb, S, and Zn in the roots and shoots of indigenous plants growing around the Khatunabad copper smelter and refinery. To determine and evaluate the degree of tolerance and strategies that plant species applied for the metal uptake, two indices, namely BCF and TF [16], were used in the phytoremediation process. The current study aimed to examine the metal removal efficiency of *Artemisia* sp., *Stipa* sp., *Launaea acanthodes*, *Peganum harmala*, and *Cousinia congesta* in heavy metals (HM)-contaminated soil near the factory. The purpose of this research was to use techniques, indicators, or factors that can show the capability of native plants in accumulating heavy metals in the Khatunabad plain. The following approaches were considered in the evaluation process: Firstly, the element accumulation value of the plants in the sampling points was measured, and the MAI was then applied for identifying the hyperaccumulator plant species and mapping the accumulation of HMs in the Khatunabad plain. The bioconcentration factor (BCF) was applied to compare the plant species capability in accumulating heavy metals in roots. Furthermore, the translocation factor (TF) was measured to compare the values of metal translocation in the plant from the root to the respiratory organs. The plant species were compared with each other based on the TF, BCF, and MAI factors to assess the plants' potential in phytoextraction and phytostabilization of the trace elements. Finally, the results of applying various factors on different elements were presented and evaluated for all the native hyperaccumulator species in the area.

## 2. Materials and Methods

### 2.1. Study Area

The Khatunabad plain in the Kerman province of Iran was selected as the case study. This plain is located at longitude 55°08′ N and latitude 30°08′ E. It is one of the famous Iranian plains for diverse herbal species and widely developed agriculture and livestock farming. The construction of the copper smelter and refinery has created multiple economic and social issues for the local people. Figure 1 shows the map of the study area, several real images from the vicinity, and the vegetation and soil destruction through heavy metal contamination by the smelter and refinery.

The altitude of the Khatunabad copper smelter and refinery is about 1870 m above sea level. The Khatunabad plain is surrounded by two mountains on the northern and eastern sides. The factory is situated on a broad plain with diverse types of plants and animals. In addition, residential areas, wildlife, national parks, environmentally protected areas, and agricultural lands are located in the surrounding regions of the KHCSR [52].

The Khatunabad plain has a dry climate in the center and a temperate climate in the margins. The average annual temperature, rainfall, and evaporation in the plain are 15.1 °C, 162 mm, and 2462 mm, respectively. The average monthly temperature in the region varies between 4 and 27 °C, with the maximum and minimum temperatures of 40 and −17 °C. The main direction of winds in the area is south-southwest, with speed varying between 0 and 25 m/s [53].

The Khatunabad copper smelter and refinery are located near the farmlands, croplands, and pastures. After the first contaminations, some modifications were implemented on the electro-filters of the factory to decrease the quantity of emitted gases and particles. However, the intensity of anthropogenic pollution is still significant, which has caused concerns around the factory.

Previous studies have shown a direct effect of the Khatunabad copper smelter on the contamination of soil and air in the area [54]. Unfortunately, disease outbreaks of unknown etiology have been reported in Shahrebabak city, which is near the KHCSR. The number of infected sheep increases in the vicinity of the smelter [55]. Moreover, high copper concentrations found in sheep livers and kidneys of 50 sheep herds in the Khatunabad area have revealed chronic toxicity. This pollution has posed severe public economic and health losses in the region [54].

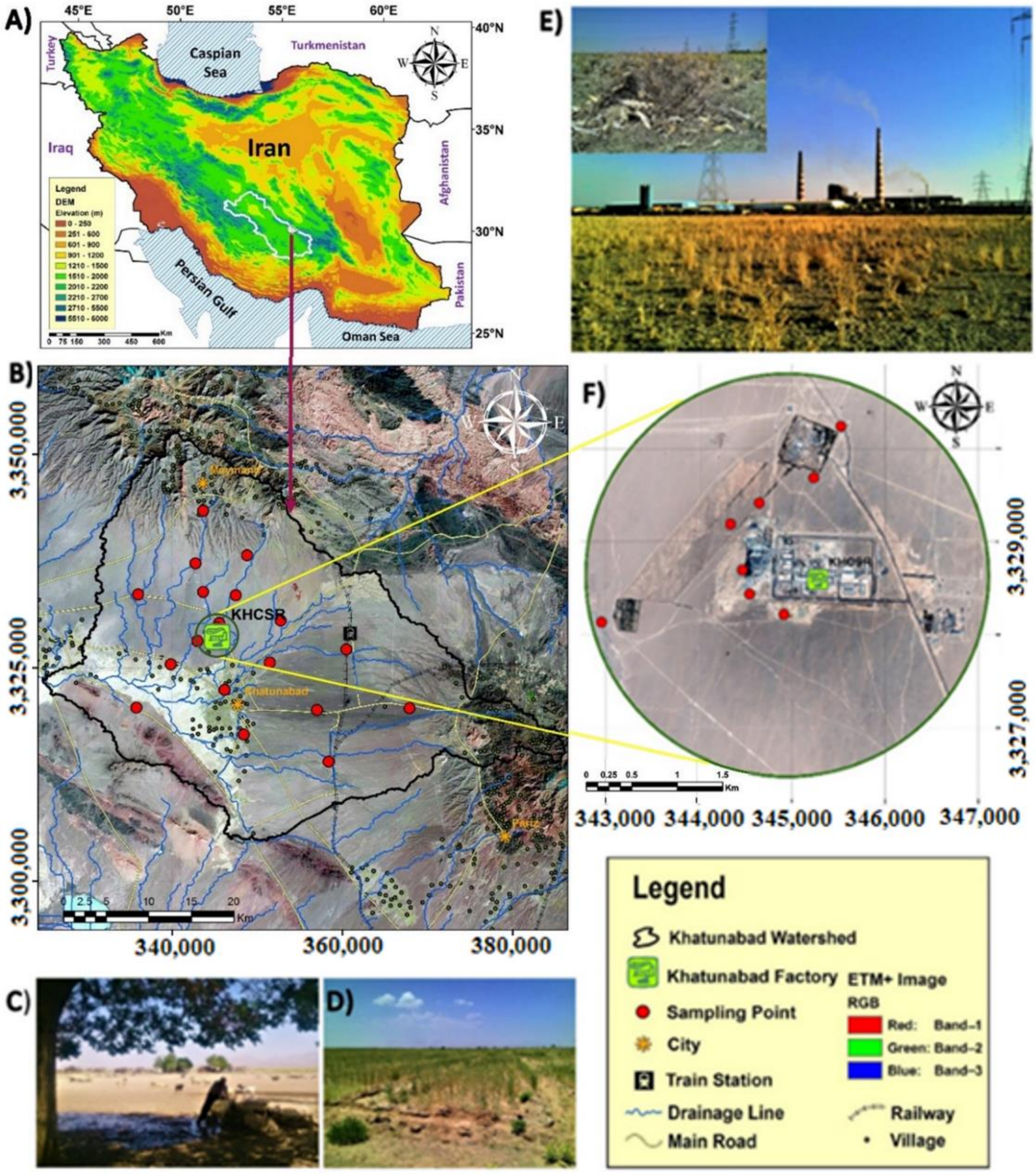


**Figure 1.** Location of the study area in Iran (**A**), detail map of the Khatunabad area and sampling points (satellite image from Landsat 8) (**B**), livestock around the smelter (**C**), farming around the smelter (**D**), two main towers of the smelter and vegetation destruction through heavy metal contamination (**E**), and zoom view of the copper smelter and refinery (**F**).

*2.2. Plants Species*

The plant species selected are *Artemisia* sp., *Stipa* sp., *Launaea acanthodes*, *Peganum harmala*, and *Cousinia congesta*. These plants were present at all the sampling stations and had a high distribution in the vicinity of the smelter and refinery. Figure 2 shows the selected plant species.

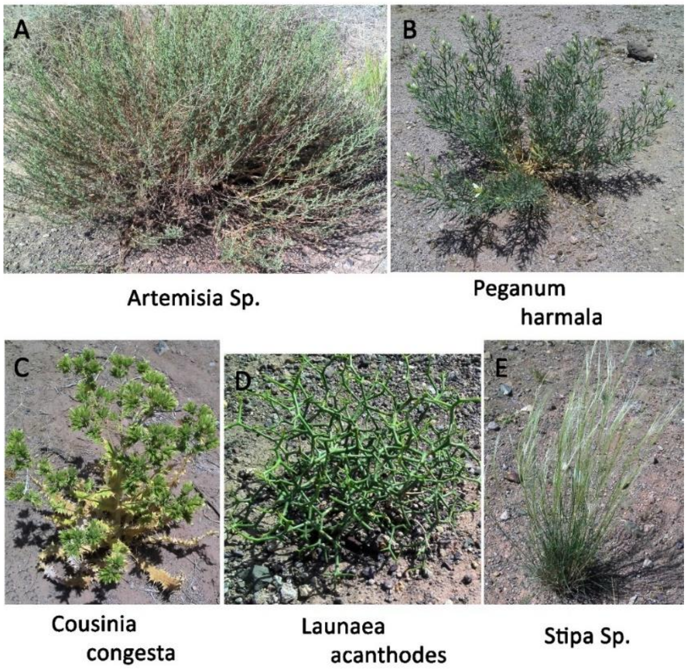


**Figure 2.** Selected plant species: *Artemisia* sp. (**A**), *Peganum harmala* (**B**), *Cousinia congesta* (**C**), *Launaea acanthodes* (**D**), and *Stipa* sp. (**E**).

*2.3. Sampling and Methods of Analysis*

A field survey was carried out along the factory watershed. The samples were collected from highly polluted soils in urban, industrial, agricultural, and farming lands. Figure 1 shows the map of sampling points. The soil samples were collected at 0–10 cm depths. Then, the dried samples were subjected to geochemical analyses at the Zarazma Mineral Studies Company, Tehran, Iran.

All soil samples were sieved down to 75 μm using a 200-mesh sieve. Then, they were subjected to a weak aqua regia digestion (WAD) technique. In this method, instead of digesting the samples with a 3:1 mixture of hydrochloric (HCl) and nitric ($HNO_3$) acids, the process was carried out using a 1:1 mixture of HCl-$HNO_3$ acids plus one unit of distilled water. The main aim was to dissolve and digest the environmentally hazardous part of the soil. By using the WAD technique, the soluble part of the soil can be extracted. The metals and toxins that threaten the environment are generally attached to clay particles of the soil, and this portion can be dissolved with this weak acid. The elements that are attached to the silica part of the soil are not environmentally hazardous, because they are not easily soluble or mobile. It should be noted if the standard aqua regia digestion (SAD) or the HF/multi-acid digestion (HMAD) techniques are used, the non-hazardous part of the soil is also digested, which would not provide an accurate perspective on the contaminated area. Accordingly, we used the WAD technique.

A principal component analysis (PCA) was conducted on the soil samples using SPSS software to identify natural or anthropogenic sources of the elements (Figure 3). Multivariate statistical analyses showed a natural source for elements Al, Ce, Co, Mg, Mn, Ni, P, Sc, Ti, V, Y, Yb, and Zr and an anthropogenic source for elements As, Cd, Cu, Mo, Pb, Sb, and Zn. Based on multivariable statistical analyses, As, Cu, Mn, Mo, Ni, Pb, S, and Zn were selected for further analysis and finding suitable native hyperaccumulator plants. In all computations, we used the concentrations of these eight elements. Afterward, we carried out the digital soil mapping process for the Khatunabad plain to identify the most hazardous and contaminated parts of the study plain. Finally, the plant species sampling process was conducted. Based on the spatial zoning map of the soil pollution status, several samples were taken from the plant species (root and aerial organs) on the most contaminated points of the plain (Figure 1). In other parts of the plain, the samples were taken only from respiratory organs. In this study, a total of 50 plant samples of 5 species were collected from 15 locations at the study site. These plant samples were dried for ten days at 150 °C. Afterward, the analysis of the prepared samples was carried out using an inductively coupled plasma mass spectrometry (ICP-MS) technique at the Zarazma Mineral Studies Company, Tehran, Iran.

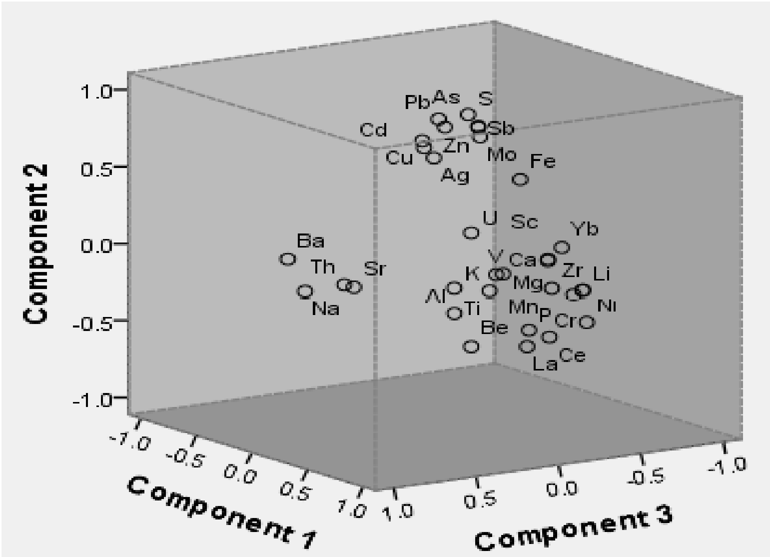


**Figure 3.** Result of principal component analysis (PCA) in soil samples that shows the difference between natural origin and anthropogenic origin of different elements.

### *2.4. Methods of Pollution Assessment of Heavy Metals*

Compared to normal plant species growing in soils with background metal concentrations, hyperaccumulator plants concentrate the metals by two or three orders of magnitude. In addition, hyperaccumulators accumulate metal concentrations about 10 to 100 times more in comparison to other plants growing in metal-contaminated soils [14].

By definition, when a plant concentrates 1000 mg/kg dry weight of metals such as Ni, Co, Cu, Pb, and Zn in its aboveground tissues, it can be called a hyperaccumulator [42]. However, the threshold value for Mn and Zn is 10,000 mg/kg [56], and for Cd, it is greater than or equal to 100 mg/kg [16].

To analyze and compare the heavy metal uptake values of the studied native plant species and identify the hyperaccumulator species, three factors, namely MAI, BCF, and TF, were computed. The translocation factor (TF) is an index comparing the metal concentration in plant roots against that in plant shoots. A shoot-to-root metal concentration ratio of more than 1 was used to characterize hyperaccumulators. The plants that are not hyperaccumulators usually concentrate the metals more in the roots than in the shoots. Several studies [57] have been conducted to investigate the bioaccumulation factor (BF) as an index for the classification of hyperaccumulator species. In addition, the BF refers to the plant metal concentration against the soil metal concentration. For a hyperaccumulator plant, the BF is higher than 1 [58].

In this study, different indices were used for identifying the native hyperaccumulator plant among five plant species in the vicinity of the factory. The systematic determination of a native hyperaccumulator was the main purpose of the current research.

### *2.5. Metal Accumulation Index (MAI)*

Environmental pollution caused by heavy metals in multi-component soil systems has become a widespread occurrence; compared to the effects of a single-component system, the interactions between the metals bring complexity to the ecosystems [59]. In order to evaluate pollution problems in multi-component soil systems, different indices can be used. In addition, plant leaves absorb and accumulate different elements at the same time. Hence, to evaluate the overall performance of HM accumulation in the plants, the metal accumulation index (MAI) was developed by Liu et al. [60,61].

$$MAI = \frac{1}{N}\sum_{j=0}^{N}\frac{X_j}{\delta X_j} \quad (1)$$

where $N$ represents the total number of metals analyzed; $X_j$ is the mean concentration of an element, and $\delta X_j$ denotes its standard deviation.

The MAI has been used for evaluating the metal concentration in the soil and plants and selecting possible hyperaccumulators.

*2.6. Bioconcentration Factor (BCF)*

The bioconcentration factor (BCF) was used to evaluate the ability of plants to accumulate metals from contaminated soils. BCF is defined as the ratio of HM concentration in the plant (both root and shoot) to HM concentration in the contaminated soil [56].

$$BCF = \frac{C_{Plant}}{C_{Soil}} \quad (2)$$

where both concentrations $C_{plant}$ and $C_{soil}$ are in mg/kg of dry weight. This ratio was applied to assess how plants potentially accumulate heavy metals [13].

*2.7. Translocation Factor (TF)*

The TF index was defined for measuring a plant's capability to translocate metals from the roots to the shoots. Alaboudi et al. [62] defined the TF as the ratio of metal concentration in the aerial part of the plant to the metal concentration in the plant's root.

$$TF = \frac{C_{Aerial}}{C_{Root}} \quad (3)$$

where $C_{aerial}$ is the concentration in the aerial part, and $C_{Roots}$ denotes the HM concentration in plant roots, both in mg/kg of dry weight. The TF index evaluates the ability of plants to transfer heavy metals from soil to the respiratory parts. A TF value of lower than 1 indicates that the HM concentration is in the root, whereas a TF value higher than 1 shows that the concentration is in the respiratory parts [61].

Phytoextraction consistently demands the translocation of heavy metals to the plant's shoots, which are the harvestable parts of the plant. The capability of different plants in absorbing HMs from soils and translocating them to the respiratory parts can be evaluated using the BCF and TF indices. Tolerant plants resist the transfer of metals between soils and roots or between roots and shoots, and therefore they accumulate lower HM concentrations in their biomass. However, hyperaccumulators continuously absorb HMs from the soil and translocate them into the respiratory organs. When both TF and BCF values are greater than 1, the plant is appropriate for phytoextraction [63].

It should be noted that sometimes the BCF value is less than 1, but this is related to a large amount of the HMs in soil rather than being related to the plant species. For example, in soils originating from ultramafic rocks, the amount of Ni reaches 3000 mg/kg, and in this situation, the amount of Ni in plants can even be 2000 mg/kg, but the BCF value would be less than 1. In another case, a plant might be very efficient in sequestration while it has low levels of absorbed HMs in its biomass (e.g., Zn). In this case, the BCF value is very high, but the plant does not absorb a considerable amount of HM contents. BCF is a valuable index for comparing the plant's behavior in homogenized soils or hydroponic culture; however, it is not a suitable index for comparing foliar metal concentrations [64]. In summary, for quantifying and measuring the relative difference in the bioavailability of heavy metals to plants, BCF is considered a reliable and valid method [65].

## 3. Results and Discussion

### *3.1. Soil Properties*

The soil samples taken from the plain had no distinct chemical difference. As Table 1 shows, the soil contained high contents of silica and aluminosilicate (82%) and calcium and iron oxides (~7%). The soil had an alkaline pH value of 9.03 and a slight amount of sulfate ions. Table 2 presents the average concentration of chemical compositions in the area of interest compared to global standards.

**Table 1.** Physical and chemical characteristics of the soil samples (anions, oxides, pH, and EC).

| Oxides (%) | | | | Anions (ppm) | |
|---|---|---|---|---|---|
| $SiO_2$ | 69.05 | MnO | 0.06 | $HCO_3^{(1-)}$ | 9.0 |
| $Al_2O_3$ | 13.48 | $Na_2O$ | 3.18 | $CO_3^{(2-)}$ | 2.0 |
| BaO | 0.07 | $P_2O_5$ | 0.10 | $F^{(-)}$ | 2.6 |
| CaO | 4.30 | $SO_3$ | 0.07 | $Cl^{(-)}$ | 26.7 |
| $Fe_2O_3$ | 3.37 | $TiO_2$ | 0.40 | $Br^{(-)}$ | < |
| FeO | 0.63 | $Cr_2O_3$ | 0.01 | $SO_4^{(2-)}$ | 119.9 |
| K2O | 2.19 | Sr | 0.06 | $NO_2^{(-)}$ | < |
| MgO | 1.18 | LOI | 2.48 | $NO_3^{(-)}$ | < |
| Soil pH | 9.03 | Soil Ec | 164.5 ms | $PO_4^{(3-)}$ | < |

**Table 2.** The metal content of the soil with world standard limitations (* means not provided).

| HMs (Water-Soluble and Exchangeable Fraction) | Concentration (ppm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | As | Cd | Cu | Mo | Pb | Sb | Zn |
| The average concentration in the study area | 276 | 7.1 | 5444 | 26.6 | 253.7 | 14.1 | 421.5 |
| The average concentration in soil [66] | 0.1–15 | 0.01–2 | 15–40 | 1–2 | 15–30 | * | 50–100 |
| The maximum concentration in extractable resources | * | * | 250 | 101 | 1200 | * | 900 |
| Metal concentration threshold in soil [67] | 15 | 1 | 75 | 2 | 100 | * | 200 |
| Threshold for uncontaminated soil [68] | <3 | * | <25 | * | <40 | * | <90 |
| Threshold for contaminated soil [68] | 3–8 | * | 25–50 | * | 40–60 | * | 90–200 |
| Threshold for highly contaminated soil [68] | >8 | >6 | >50 | * | >60 | * | >90 |

Table 3 presents the results of the XRD analysis on the soil. As shown, quartz and aluminosilicate minerals such as labradorite and albite are the major minerals in the soil. The sample contains about 4% calcite and 6.7% clay minerals, including 2.8% illite, 2.4% montmorillonite, and 1.5% kaolinite. Unlike the chemical characteristics of the soil over the plain, the concentrations of heavy metals in the sampling points show a considerable difference (Table 3).

**Table 3.** Characteristics of the soil samples of the area (properties and XRD analysis).

| Mineral Name | Chemical Equation | Percentage (Semi-Quantitative) |
|---|---|---|
| Quartz | $SiO_2$ | 41 |
| Labradorite | $(Na_{0.4}Ca_{0.6})Al_{1.6}Si_{2.4}O_8$ | 23.3 |
| Albite (calcian-ordered) | $(Na, Ca)(Si, Al)_4O_8$ | 17.1 |
| Calcite, syn | $CaCO_3$ | 3.6 |
| Chlorite | $(Mg, Fe)_5(Al, Si)_5O_{10}(OH)_8$ | 3.2 |
| Illite | $K(AlFe)_2AlSi_3O_{10}(OH)_2{\cdot}H_2O$ | 2.8 |
| Magnetite | $(Fe, Mg)(Al, Cr, Fe, Ti)_2O_4$ | 2.7 |
| Montmorillonite | $(Al(OH)_2)_{0.33}Al_2(Si_{3.67}Al_{0.33}O_{10})(OH)_2$ | 2.4 |
| Magnesio-hornblende | $(Ca, Na)_{2.26}(Mg, Fe, Al)_{5.15}(Si, Al)_8O_{22}(OH)_2$ | 1.8 |
| Kaolinite | $Al_2Si_2O_5(OH)_4$ | 1.5 |
| Hematite, syn | $Fe_2O_3$ | 0.6 |
| Kaolinite | $Al_2Si_2O_5(OH)_4/Al_2O_3{\cdot}2SiO_22H_2O$ | 0 |

### 3.2. Metal Accumulation in Plant Tissue (MAI)

Plants can potentially accumulate heavy metals from the surrounding environment to levels higher than those in the soil. However, different plant species have differences in their ability to accumulate toxic metals [69]. Herein, the MAI and the concentration value of the elements were used to compare the sampled plants. Accordingly, the heavy metal concentrations were measured in the respiratory organs of 50 plants (Table 4).

**Table 4.** Determining the MAI based on the concentration of different elements (mg/kg) in the plant species.

| MAI | Mean/Standard Deviation (mg/kg) | | | | | | | | Species Name |
|---|---|---|---|---|---|---|---|---|---|
| | As | Cu | Mn | Mo | Ni | Pb | S | Zn | |
| 1.29 | 4.3 ± 9.4<br>0.46 | 28.2 ± 19.2<br>1.47 | 47 ± 48.9<br>0.96 | 1.0 ± 1.4<br>0.72 | 2.3 ± 1.0<br>2.34 | 36.1 ± 33.8<br>1.07 | 2847 ± 1067<br>2.67 | 54.7 ± 88.7<br>0.62 | *Cousinia congesta* |
| 1.67 | 3.9 ± 9.3<br>0.42 | 36.6 ± 32.9<br>1.11 | 49.7 ± 40.5<br>1.23 | 0.6 ± 0.4<br>1.52 | 1.5 ± 0.7<br>2.05 | 24.7 ± 17.1<br>1.45 | 7045 ± 1486<br>4.74 | 45.4 ± 52.7<br>0.86 | *Launaea acanthodes* |
| 3.21 | 2.2 ± 3.6<br>0.61 | 32 ± 11.8<br>2.72 | 37.3 ± 5.5<br>6.82 | 0.5 ± 0.2<br>2.63 | 1.6 ± 0.4<br>4.26 | 12.3 ± 7.0<br>1.75 | 1930 ± 435<br>4.44 | 18.9 ± 7.6<br>2.48 | *Artemisia* sp. |
| 1.8 | 4.7 ± 10.8<br>0.43 | 42.3 ± 41.7<br>1.01 | 76.5 ± 23.4<br>3.28 | 1 ± 1.1<br>0.87 | 2.9 ± 0.9<br>3.29 | 29.3 ± 31.8<br>0.92 | 1267 ± 443<br>2.86 | 27.7 ± 15.9<br>1.74 | *Stipa* sp. |
| 1.75 | 5.4 ± 12.9<br>0.42 | 33.1 ± 37.9<br>0.87 | 106 ± 21<br>5.03 | 1.0 ± 1.0<br>0.96 | 2.4 ± 1.8<br>1.29 | 19.3 ± 16.7<br>1.16 | 5798 ± 3296<br>1.76 | 19.2 ± 7.6<br>2.51 | *Peganum harmala* |
| 3.3 | 13.3 ± 7.8<br>1.7 | 66.4 ± 69.0<br>1 | 609.8 ± 168.7<br>3.6 | 1.2 ± 0.2<br>7.1 | 29.1 ± 9.1<br>3.2 | 23.0 ± 9.0<br>2.6 | 297.3 ± 103.7<br>2.9 | 70.0 ± 16.9<br>4.1 | Soil |

In Table 4, for each plant species, the first row contains two values. The first value is the average concentration, and the second one is the standard deviation (SD). The second row provides the division of the mean value by the standard deviation. Finally, the last column of the table presents the MAI of each plant species, which is the average of all measured values divided by the standard deviation of the element in the plant. As Table 4 shows, the MAI for none of the plants exceeds the MAI of the soil samples taken in the area. In other words, none of the plants can be considered hyperaccumulators. Among these five species, *Artemisia* sp. has the highest MAI, followed by *Stipa* sp., *Peganum harmala*, *Launaea acanthodes*, and *Cousinia congesta*. Table 4 shows that the highest MAI value for elements Cu, Mn, Mo, Ni, As, and Pb belongs to *Artemisia* sp. In addition, *Peganum harmala* has the first rank for Zn, and *Launaea acanthodes* has the highest MAI value for S.

Moreover, the MAI for each sampling station was obtained based on the uptake value of each plant in that station. The zoning map of the uptake values of plants was drawn based on the MAI (Figure 4). As Figure 4 presents, unexpectedly, the highest MAI values do not belong to station 7 (S7), which is in close proximity to the factory. The highest MAI values were observed at stations 15, 1, and 3. These stations are located in the west and southwest of the factory. It can be concluded that the MAI values can be attributed to the wind direction and the distance that chimney dust falls on the ground.

### 3.3. Bioconcentration Factor (BCF) in Plant Species

BCF contributes to evaluating a plant's ability to translocate heavy metals from soils to plant organs. BCF is defined as the ratio of HM content in plant organs to the ratio of HMs in the soil [10]. Table 5 presents the BCF values for the plant species. The average BCF value of all elements in the last column of the table was used to compare the bioavailability values for each native plant species.

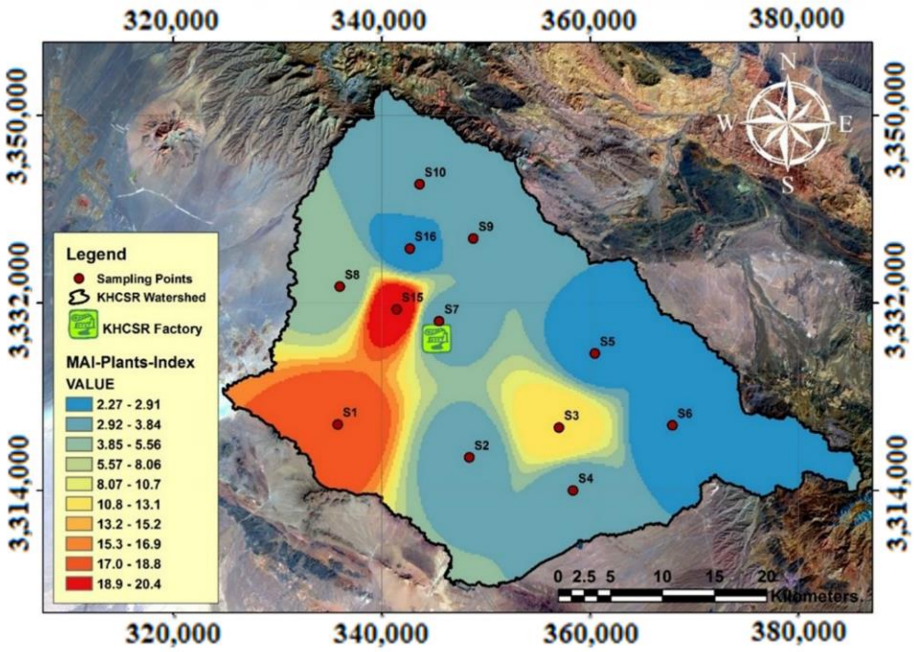


**Figure 4.** The zoning map of plant uptake values based on the MAI in the Khatunabad plain.

**Table 5.** The bioavailability index of the sampled native plants for the most polluted station of the different elements.

| Plants/Elements | Bioconcentration Factor (BCF) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | As | Cu | Mn | Mo | Ni | Pb | S | Zn | Average |
| *Cousinia congesta* | 0.73 | 0.16 | 0.02 | 1.35 | 0.06 | 1.26 | 5.39 | 0.19 | 1.15 |
| *Launaea acanthodes* | 1.47 | 0.32 | 0.05 | 0.75 | 0.06 | 0.32 | 10.02 | 0.38 | 1.67 |
| *Artemisia* sp. | 0.89 | 0.42 | 0.03 | 0.41 | 0.07 | 0.34 | 6.52 | 0.08 | 1.09 |
| *Stipa* sp. | 0.79 | 0.17 | 0.12 | 0.79 | 0.12 | 0.50 | 2.28 | 0.20 | 0.62 |
| *Peganum harmala* | 0.72 | 0.25 | 0.06 | 0.25 | 0.05 | 0.14 | 3.52 | 0.16 | 0.64 |

Figure 5 presents the average BCF value of the selected native plant species. *Launaea acanthodes* has the highest ability to accumulate the elements through the roots, followed by *Cousinia congesta*, *Artemisia* sp., *Peganum harmala*, and *Stipa* sp. Note that the value of BCF is higher than 1 only in *Launaea acanthodes*, *Cousinia congesta*, and *Artemisia* sp.

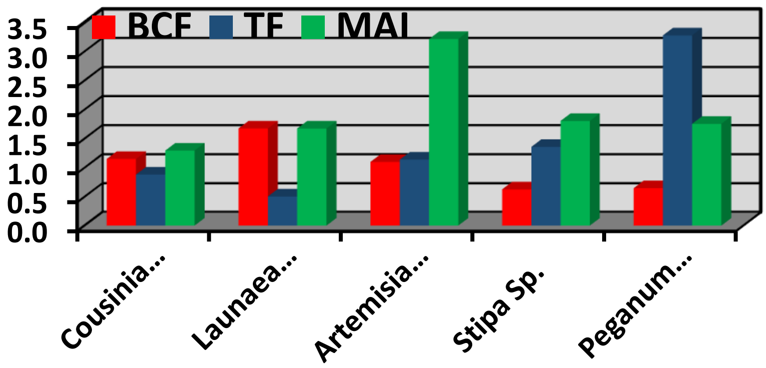


**Figure 5.** A diagram comparing the BCF, TF, and MAI values for samples of native plants based on the average of all the elements.

### 3.4. Translocation Factor (TF) in Plant Species

The TF index was applied to evaluate the ability of metals to translocate from roots to shoots. TF is defined as the ratio of aboveground biomass content to the root content of heavy metals [10]. Table 6 presents the computed TF values of different plant species for different elements. The average of computed values for all elements was used to provide to compare the translocation values in different plants. As shown in Table 6 and Figure 5, *Peganum harmala* has the highest TF value. Moreover, the TF values for *Peganum harmala*, *Stipa* sp., and *Artemisia* sp. are higher than 1.

**Table 6.** The TF values of the sampled native plants in the most contaminated station for different elements.

| **Plants/Elements** | **Translocation Factor (TF)** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **As** | **Cu** | **Mn** | **Mo** | **Ni** | **Pb** | **S** | **Zn** | **Average** |
| *Cousinia congesta* | 1.28 | 0.49 | 1.40 | 0.67 | 0.85 | 0.01 | 1.21 | 1.10 | 0.88 |
| *Launaea acanthodes* | 0.35 | 0.12 | 0.46 | 0.11 | 0.50 | 0.23 | 1.66 | 0.57 | 0.50 |
| *Artemisia* sp. | 0.85 | 1.02 | 1.32 | 0.41 | 1.07 | 0.66 | 1.88 | 1.88 | 1.14 |
| *Stipa* sp. | 1.76 | 1.84 | 0.62 | 1.82 | 0.74 | 0.79 | 1.99 | 1.29 | 1.35 |
| *Peganum harmala* | 2.13 | 0.64 | 3.79 | 5.97 | 1.98 | 0.75 | 9.64 | 1.28 | 3.27 |

Based on the computed BCF and TF values of the plant species, and since both BCF and TF values are higher than 1 only for *Artemisia* sp., this plant can be introduced as a native hyperaccumulator and can be used in the phytoextraction process. In addition, the MAI for *Artemisia* sp. is the highest value among the plants and is approximately 3.21. All three indices (BCF, TF, and MAI) confirm the capability of *Artemisia* sp. as a native hyperaccumulator plant in the study area for application in phytoremediation. Moreover, since the average computed BCF for *Cousinia congesta* is higher than 1, and the average TF values are lower than 1, it can be concluded that *Cousinia congesta* is a suitable plant for the phytostabilization process.

### 3.5. Metal Concentration in Plants

The native plant species were compared with each other based on the average values of computed factors (MAI, BCF, and TF), and the hyperaccumulator plant for phytoremediation purposes was introduced. In the following sections, different elements are investigated separately to determine the best hyperaccumulator plant species for the phytoremediation of a specific element. These computed factors can also provide valuable information on the bioavailability values of different elements.

### 3.6. Arsenic Concentration

Figure 6 shows the diagram of BCF, TF, and MAI values for arsenic. It indicates that none of the plant species simultaneously have BCF and TF factors of higher than 1 for arsenic, which means that none of the plants can be considered hyperaccumulators for As. Therefore, the plants cannot be implemented in phytoextraction.

The MAI of all the plant species, with a slight difference, is about 0.5 for arsenic, which is the lowest value of MAI among the elements in the plant species. The BCF and TF values for the *Launaea acanthodes* are respectively higher and lower than 1, showing that this species can be used for phytostabilization of the arsenic.

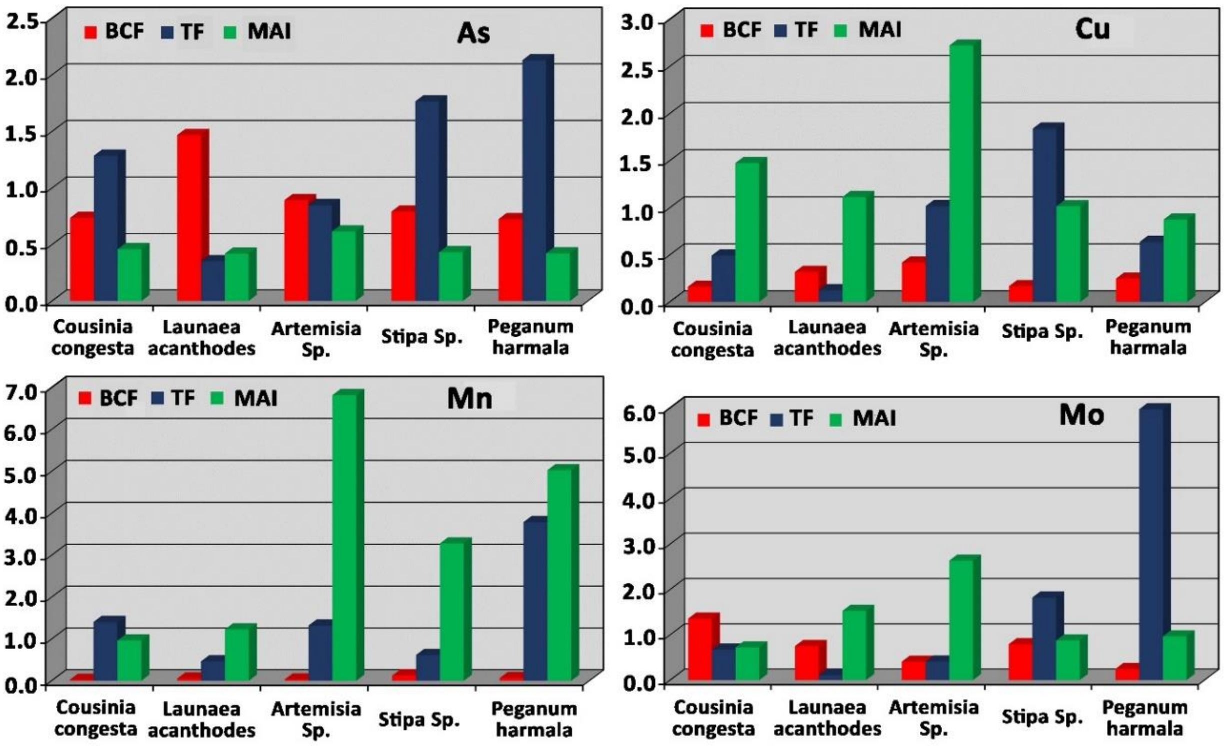


**Figure 6.** The BCF, TF, and MAI factors for Mn, Mo, Cu, and As in the native plant species.

### *3.7. Copper Concentration*

The behavior of the Cu element in the study area is complicated. The MAI in the soil of the area (MAIs) shows that the average value of Cu is 66 mg/kg while the standard deviation is 69; therefore, the final score of MAIs for Cu is the lowest amount among all the elements and is equal to 1 (MAIs = 1).

The BCF value of copper for all the plant species is slight and does not exceed 0.5, revealing the low bioavailability of copper in native plant species in the study area. In addition, the TF value is greater than 1 only for *Stipa* sp., which results from the considerable translocation of copper from roots to shoots in this plant species. Moreover, the MAI of *Artemisia* sp. is about 2.5 and higher than the others (Figure 6).

### *3.8. Molybdenum Concentration*

Molybdenum has the maximum MAI value in soil (MAIs) samples (MAIs = 7.1). As Figure 6 shows, the TF value of molybdenum in *Peganum harmala* is higher than the TF values of the other plant species, while the BCF value of *Peganum harmala* is lower than 0.5.

None of the plants have BCF and TF values higher than 1 simultaneously, which means none of them are suitable for the phytoextraction of molybdenum. The BCF value in *Cousinia congesta* exceeds 1, while its TF value is lower than 1. Therefore, this plant species can be used for the phytostabilization of Mo.

### *3.9. Manganese Concentration*

Manganese has the highest amount of average concentration in the soil samples (609 mg/kg), and after molybdenum and zinc, the value of manganese MAIs index in the soil samples is higher than others (MAIs = 3.6).

The manganese diagram (Figure 6) shows the low BCF values in all the plants, which indicates the low bioavailability of manganese. The TF value of this element exceeds 1 only in *Peganum harmala*. The accumulation value (MAI) of manganese in the *Artemisia* species is near 7, which is much higher than that of the others.

*3.10. Nickel Concentration*

The BCF value of Ni in all the plant species is lower than 0.5. In addition, the TF factor is higher than 1 only for two plant species: *Artemisia* sp. and *Peganum harmala*. The TF value in *Peganum harmala* is about 1.98 (Figure 7).

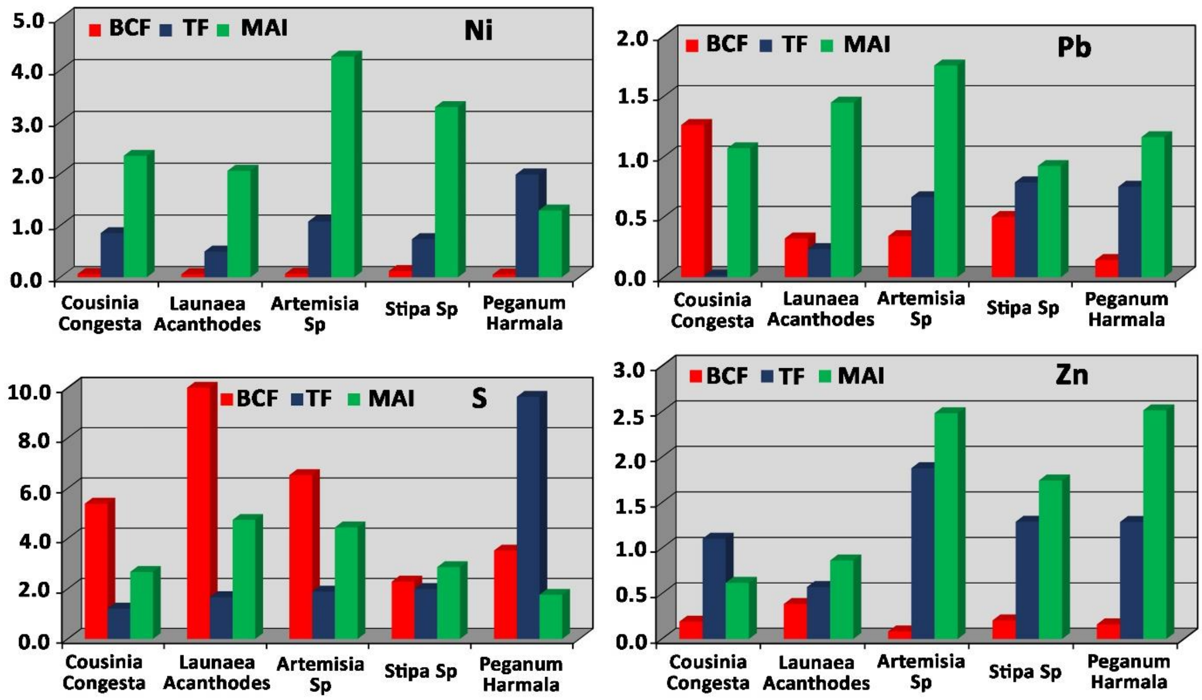


**Figure 7.** The BCF, TF, and MAI factors for Zn, S, Pb, and Ni in the native plant species.

The MAI in *Artemisia* plant species is about 4, which is higher than the values for the other plant species. Based on the TF and BCF values, none of the plants are suitable for phytoextraction and phytostabilization of nickel.

*3.11. Lead Concentration*

The accumulation value (MAI) of Pb in the studied plant species varies between 0.5 and 1.5. The highest accumulation value of lead occurs in the *Artemisia* species. The BCF value in *Cousinia congesta* is higher than 1, and the TF value is about 0 (Figure 7). Therefore, this plant can be used in the phytostabilization of Pb.

*3.12. Sulfur Concentration*

Although the MAIs value for sulfur in the soil samples is not higher than the values for the other elements, e.g., Mo, Zn, Mn, and Ni (7.1, 4.1, 3.6, and 3.2), and the average concentration of manganese is 3 times higher than sulfur, the BCF and TF values for sulfur are high (around 10).

This shows that sulfur has a significant ecological risk in the plant species of the study area. A comparison of the studied factors for sulfur (Figure 7) demonstrated that the BCF factor of the element exceeds 1 in all the plant species and is around 10 in *Launaea acanthodes*. The TF value in *Peganum harmala* is high, 9.64, which is the highest TF value among all species in the elements. The BCF and TF values of all the plants are higher than 1, and thus they can be used in the phytoextraction of sulfur.

*3.13. Zinc Concentration*

Zinc has the highest MAIs index in the soil samples (MAIs = 4.1) after molybdenum. In contrast, the TF value is higher than 1 only for *Artemisia* sp. (about 1.88). The MAI values for *Artemisia* sp. and *Peganum harmala* are higher than those for the other species (about 20.5). The computed values for zinc show that none of the plants are capable of phytoextraction and phytostabilization of this metal (Figure 7).

## 4. Conclusions

The present study screened the native plant species in the vicinity of a copper smelter and refinery to estimate their potential and suitability for phytoremediation. The accumulation of heavy metals in the roots and aerial parts of the plants was investigated using BCF and TF indices. The plant species with BCF and TF values greater than 1 had phytoextraction potential. The native plant species considered in this study were *Artemisia* sp., *Stipa* sp., *Peganum harmala*, *Cousinia congesta*, and *Launaea acanthodes*. Among the native plant species, only *Artemisia* sp. was identified as a metal hyperaccumulator. The results show that *Artemisia* sp. had a higher MAI as compared to other species, which could be due to its high biomass volume. The results further show that *Artemisia* sp. with values of 3.21, 1.09, and 1.14 for MAI, BCF, and TF, respectively, can be suitable for phytoextraction in the study area. Moreover, in the plant species *Launaea acanthodes*, the value of BCF was higher than 1 and the value of TF was less than 1, so this plant can be used in the phytoremediation of arsenic through the phytostabilization process.

It was observed that Cu, Mn, Mo, Ni, and Pb had the highest MAI values in *Artemisia* sp. The BCF factor indicates that *Launaea acanthodes* had the highest uptake value through the roots, and *Peganum harmala* had the highest TF value. Since both BCF and TF values were higher than 1 in *Artemisia* sp., this plant could be used as a hyperaccumulator plant for the phytoextraction technique. *Cousinia congesta* is introduced as a phytostabilization candidate because it showed BCF and TF values of higher and lower than 1, respectively. Moreover, the MAI of this plant was higher than those of the others.

The study of different factors for separate elements shows that these five native plant species had different performances for the various elements. The accumulation value of Mn in *Artemisia* was close to 7 and much higher than those in other plant species. The BCF value of Mo in *Cousinia congesta* was higher than 1 with a TF value lower than 1. Therefore, it is recommended that this plant is used in the phytostabilization of molybdenum. However, copper showed little bioavailability in these plant species, and for zinc, none of the plants had the potential for phytoextraction and phytostabilization.

The native plant proposed in this article can be effectively used in practical applications of phytoremediation with the aim of remediating soil contaminated by heavy metals around metal smelting factories and mining sites in southeastern Iran.

**Author Contributions:** Conceptualization, R.S., F.D.A. and P.N.; methodology, R.S. and F.D.A.; formal analysis, R.S., P.N., S.M., M.Y, and R.T.; investigation, R.S.; writing—review and editing, R.S., F.D.A., P.N., S.M., M.Y., R.T. and C.B.; funding acquisition, F.D.A. and C.B. All authors have read and agreed to the published version of the manuscript.

**Funding:** Open Access Funding by the Publication Fund of the TU Bergakademie Freiberg.

**Data Availability Statement:** Not applicable.

**Acknowledgments:** The current research is funded as part of project No. 95.10196, and the authors are very thankful for the collaboration of the R&D division of National Iranian Copper Company (NICICo). The authors greatly appreciate the MEHR laboratory of the University of Tehran for spiritual and financial support.

**Conflicts of Interest:** The authors declare that they have no conflict of interest.

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