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Full Length Research Paper

Introducing hyperaccumulator indicator plants for As, Mo, Cd, Hg, and Sb in Masjed–Daghi, Julfa (Iran)

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The aims of present study are investigation of endemic plants at Masjed-Daghi area introducing hyperaccumulator and indicator plants for As, Mo, Cd, Hg, and Sb elements and also describe the biogeochemical response pattern over Azerbaijan area. The Masjed-Daghi prospecting area is covered by Eocene flysch, andesite, trachyandesite, dacite, rhyodacite, Oligocene agglomerate, and Quaternary deposits. Previous researches reported copper porphyry mineralization and related epithermal gold veins in this area. This study presents that plants with high metal intake enabled us to obtain invaluable information about natural concentrations of chemical elements in the substrate and to recognize new potential areas for mineral prospecting. *S. inflata has* biological absorption coefficient mean exceeding or near hyperaccumulating criterion >1 for most of the elements investigated then could be as a hyperaccumulator. The indicator values belong to *S. inflata, Artemisia* sp., *Salvia* sp., *Astragalus* sp., *P. harmala*, *M. coerulea* and *Cousinia* sp.

Key words: Biogeochemical exploration, hyperaccumulator, indicator, biological absorption coefficient, Geobotany, copper porphyry, Masjed–Daghi, Julfa (Iran).

INTRODUCTION

Worldwide, distinctive plant communities are known to occur over metal-rich soils (Baker, 1981; Baker and Brooks, 1989; Krämer, 2010). The root system of plants acts as a powerful sampling mechanism because they collect solutions from a large volume of humid ground. Inorganic salts of solutions are usually deposited in the upper parts of plants.

Therefore, plants carry out two important functions in the environment where they live; they solve and intake metals and other constituents of the ground. As plants concentrate metals and other inorganic substances in their bodies, they have been used as a useful tool for biogeochemical exploration of subsurface sources (Sasmaz et al., 2006).

The biological absorption coefficient (BAC) is used to characterize the intensity of absorption of chemical elements by plants from their substrate. Kovalevsky (1995) has defined the biological absorption coefficient as follows: BAC $=C_p/C_s$ w where C_p is the concentration of an element in plant and Cs is the concentration of the same element in soil. The range of BAC values widely varies from 0.0001 to 10 (Brooks et al., 1995). If BAC values are expressed on a dry weight basis, the levels for most elements are below unity. Metal intake abilities of plants vary in large intervals, and the plants which take up high amounts of metals are defined as "hyperaccumulator plants". Criteria for "hyperaccumulator plants" are described as trace metals' contents in shoot dry matter (Au>1 mg kg-1; Cd, As >100 mg kg-1; Co, Cu, Ni, Pb >1000 mg kg-1; Mn, Zn>10,000 mg kg-1), the ability to store heavy metals in aboveground parts is 10-500 times more than in usual plants, and BAC is >1(Ensley, 2000; Lasat, 2002; Fayiga et al., 2004).

Hyperaccumulators usually have a low biomass because they use more energy in the necessary mechanisms to adapt to the metal high concentrations in tissues (Kabata - Pendias 2001).Baker (1981) divided plant species into three groups (Table 1) in terms of their aboveground metal concentrations and in relation to the metal's concentrations in soil (BAC).

Hyperaccumulator plants have been severely considered for reclamation of contaminated lands due to mining and other industrial activities (Desouza et al., 2000, Wei et al., 2002, Ozturk et al., 2003). Plant species that exclude or accumulate metals in their biomass are of

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Table 1. Baker classification of BAC values (Baker (1981)

	Group name	BAC values
1	Excluders	Very low
2	Indicators	Relatively constant
3	Hyperaccumulators	High

Table 2. Perel’man classification of BAC values Perel’man (1966)

	Group name	BAC values
1	Intensive	10-100
2	Strong	1.-10
3	Intermediate	0.1-1
4	Weak	0.01-0.1
5	Very weak	0.001-0.01

considerable interest in biogeochemical prospecting, mine site rehabilitation and phytomining (Sheoran et al., 2009; Jiménez et al., 2011). The variability in plant species may play a major role in this division because of their BAC or biomass (Yeh et al. 2009). Also plants have been classified by Perel’man (1966) into five groups in terms of BAC values (Table 2).

The aims of present study are investigation of endemic plants in Masjed-Daghi area introducing hyperaccumulator and indicator plants for arsenic, molybdenum, cadmium, mercury, and antimony describe the biogeochemical response pattern over a known "Au-Cu" mineralized site in the study area and finally purpose them for using in phytoremediation.

The Study Area

Masjed-Daghi is located in the northwest of Iran having an area about 2.4 km (east- west) by 1.2 km (north-south) between northern latitudes 38° 52' 01"-38° 53' 03" and eastern longitudes 45° 55' 35"- 45° 57' 25" (Figure 1).

The study area consists of Cenozoic and Quaternary rocks, their lithologies are as follows; Eocene flysch, andesite, trachyandesite, dacite, rhyodacite, Oligocene agglomerate and Quaternary deposits as traces, sand dune and river flood sediments (Akbarpour and Mohammadi, 2003).

In previous researches gold, copper, lead, and zinc mineralization were reported in this area. The Masjed-Daghi deposit is porphyry copper and porphyry-related medium-sulfidation copper- gold veins (Mohammadi, 2004; Akbarpour, 2005).

Genesis of the deposit is magmatic-hydrothermal and its paragenesis minerals are chalcopyrite, barite, malachite, azurite, galena and gold. The highest value of Au in one of the silicic veins (east –west) is 40 g /ton, the average value is 2.5 g / ton and its tonnage is 1 ton (Mohammadi, 2004).

Climate

The climate of study area is semi-arid with average annual rainfall about 192 mm in Kiamaki Mountain mostly falling in winter and to some extent in autumn and early spring. The daily maximum temperature of both areas reaches 50.8 °C near the Aras River and a minimum of 3 °C (Synoptic station of Julfa, Azerbaijan; Iranian Meteorological Org, 2011; Najafi, 2002).

Vegetation

Vegetation around the Aras River in both coasts of Iran and Azerbaijan (Nakhjavan) varies along the climatic gradients and consists of thorns, bushes and in somewhere Tamarix (After http://www.iauj.ac.ir/pages.aspx?id=337, 2010). Based on current systematic studies implemented by Zare and Salmaki (Tehran University, Iran), vegetation of studied area comprises the following plants; spurge (*Euphorbia myrsinites*), S*enecio* (*Senecio glaucus*), spinach (Chenopodiaceae), chamomile (*Anthemis odontostephana*), polygonome (*Pteropyrum* sp.), onion (*Allium umbilicatum*), astragalus (*Astragalus* sp.), Camelthorn (*Alhaji pseudoalhaji*), *Lepidium vesicarium*, *Sterigmostemum sulphureum*, harme(*Peganun harmala*), *Stachys inflata*, *Torilis stocksiana*, *Biebersteinia multifida*, *mint (Nepeta meyeri)*, solanum (*Lysium depressum*), borage*(Moltkia coerulea)*, *Artemisia* sp., *Crepis* sp., *Cousinia* sp., *Dorema* sp., *Salvia* sp., Madder (Cruciata

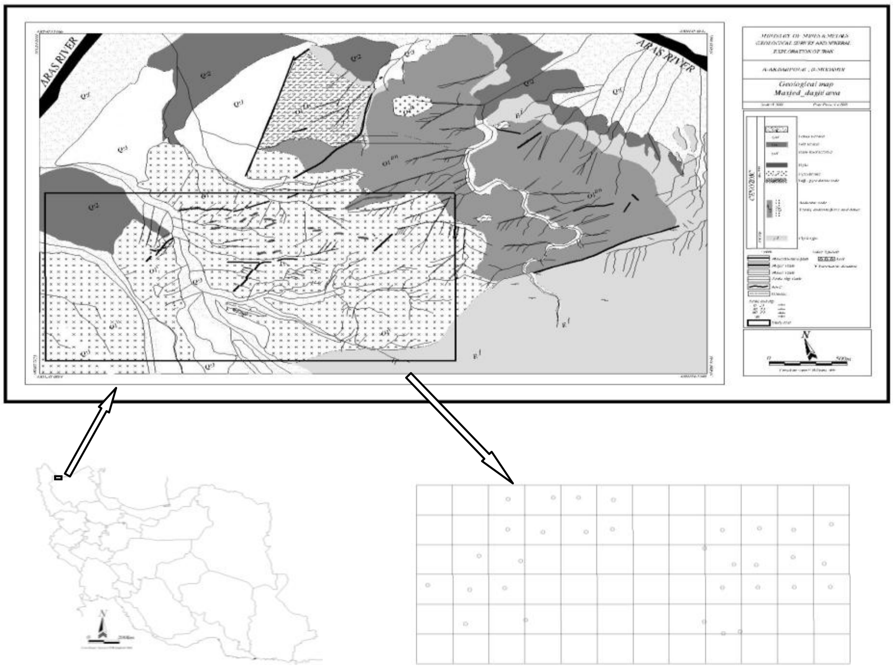

Figure 1. Geological map of Masjed-Daghi area in scale 1:5,000 (after Akbarpour and Mohammadi, 2003) and sample locations in current study

sp.), *Acantholimon* sp.

MATERIALS AND METHODS

Sampling

In this study, based on data from anomalous areas introduced by Akbarpour (2005) and optimum application of available data (former geochemical exploration, vegetation plus geological and topographical maps) a sampling grid was designed (200m × 200 m; Figure 1). The average sampling density is 1 sample per 0.09 km2 for soil samples and 1 sample per 0.03 km2 for plant samples, but it was considerably increased in areas where a steep gradient in changing lithology could be expected or low density of vegetation, and decreased in areas with nearly homogeneous bedrock or high density and vegetation diversity.

Soil and plant samples were collected during comprehensive field trips during June 2009 across the study areas. In Masjed–Daghi area with known porphyry system of mineralization for copper and gold, such simple orientation can be conducted to determine whether a biological response is obtained in common plants.

Sampling was done in two parts, including soil and plant. At least two individuals of each plant species were collected within the sampling area; biogeochemical samples and geobotanical samples.

In this project, 31 sampling sites were selected comprising a soil sample, several geobotanical and biogeochemical samples in each site. Totally, 31 soil samples, 119 geobotanical samples and 119 biogeochemical samples were collected from Masjed-Daghi area.

Soil Samples

Soil sampling is needed to determine BAC values and pH. Soil were sampled from 10- 30 cm depth (depending on depth of plant's roots) to avoid recent transported material. Weight of each sample was about 250 g, sufficient to yield 30 to 50g of representative sample powder to use during the analytical studies (Rose et al., 1979; Thornton, 1983). The samples were excavated with a spade, sieved by -80mesh sieve, and placed in a plastic bag.

The soil pH for most sites varies between 7 and 7.8. The soil samples were sent to ALS laboratory, Canada for analysis by inductively coupled plasma mass spectrometry (ICP-MS) and ICP-atomic emission spectroscopy (AES) methods and using "Aqua regia" digestion methods. Elements were determined by a Perkin Elmer Elan9000 ICP-MS and Agilent ICP-AES instruments. To analyze Au-ICP21, Aligent ICP-AES was employed.

Plant Samples

Plant samples were collected from the same location, like soil samples. The selection of plants was limited to those that were readily identified, dominant, and widespread in Masjed–Daghi area. Plants had similar size, age, and health

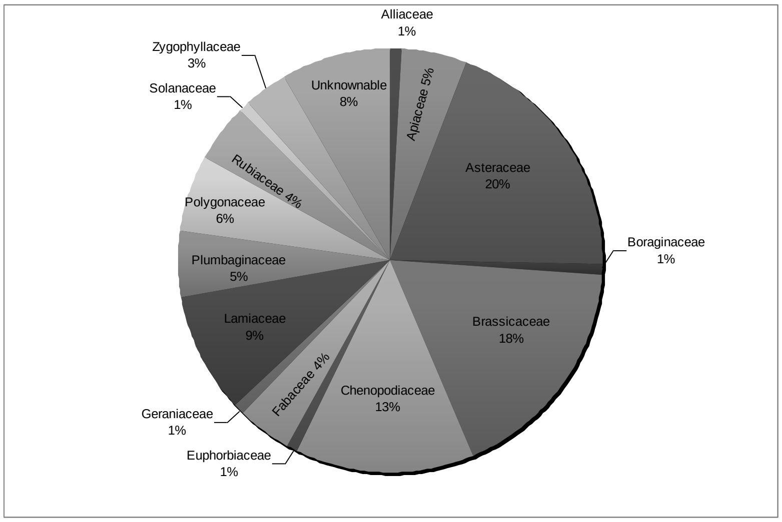

Figure 2. Diagram showing the percent of plant samples belonging to 15 families

so that results were comparable. The younger and upper leaves and twigs of plant were preferred and a pruning hook may be useful. Older and unhealthy plants should not be sampled. Besides, each plant organ has a different capacity to store nutrients and metals and therefore, valid conclusions may only be drawn by comparing the same plant tissues (Smith, 1984; Dunn, 1995; Ernst, 1996).

For this research twig, leaves and roots for herbs, and twig and leaves for shrubs and bushes were sampled (biogeochemical sample). As the nutrient levels have been reported to vary between sun and shade leaves (Salisbury and Arose, 1978; Brooks et al., 1995), to minimize these problems, it was necessary to sample from different direction around the plant to obtain an estimation of whole plant chemistry (about large plants). The samples were collected from different sites to investigate geochemical changes in different areas. A sample of between 100-200g was collected. The collected samples were stored in Kraft bags to avoid mold development.

Plant Sample Processing

The sample preparation procedure comprises washing, drying, and grinding. The plant samples were then oven dried at 60- 70 °C for 48 hours to obtain constant weight. High temperature (above 70 °C) and drying for long periods (more than 48 h) were avoided, as it cause significant losses in total weight. Conversely, temperatures below 70°C will not halt metabolic activity and mold development that can alter element abundances, particularly if the samples are initially damp (Mac Naeidhe, 1995).

The dried samples were ground to a fine powder using a rotating stainless steel blade mill (Breville® Coffee ‘n’ Spice Grinder), and then the milled samples were split for duplicate analyses. The grinder was cleaned with ethanol and compressed air between each sample to ensure that all traces of the previous sample were removed. The grinder was then pre-contaminated with a small amount of the ensuing sample then cleaned again before grinding the sample for analysis. The samples were analyzed as a whole were subjected to a cold, concentrated nitric acid digest overnight, then a concentrated perchloric acid attack to fully dissolve the tissues ("Aqua regia" digestion methods). Analysis was by ICP-MS (ALS Analytical Labs, Canada). Elements were determined by the technique: analytical method of ICP-MS: Perkin Elmer Elan 9000 ICP-MS instrument.

At least 2 samples were collected from a sampling site; a biogeochemical sample and a geobotanical sample. After drying, Geobotanical sample for identification only were kept in a plant press 3 weeks and separated from those used for analysis. Plant identification was confirmed by the Department of Botany, University of Tehran, Iran**.**

Quality Assurance and Quality Control

A rigorous data quality control (quality assurance and quality control) was effected by the insertion of reagent blanks, duplicate samples and inhouse-calculated error for duplicate plant samples shows accuracy about 95% for all elements, but Thompson-Howarth (1978) duplicate error plot for duplicate samples shows accuracy about 90% for Cd; 90% for Mo; 80% for As, Sb; and less than 80% for Hg. For soil samples calculated errors shows about 90% for As, Cd, Mo; 80% for Sb and less than 80% for Hg.

RESULTS AND DISCUSSION

Most plants were sampled in study area belonging to 15 families. The families belong to: Alliaceae, Apiaceae, Asteraceae, Boraginaceae, Brassicaceae, Chenopodiaceae, Euphorbiaceae, Fabaceae,

Table 3. Identification list of plant samples in the study area

Samp No.	***Elevate(m)***	***Abundance***	***Sample Organ***	***PH***	***Growth form***	***Scientific name***	***Family***
84(1)	1320	aboundent	twig & foliage	7.1	perennial herb	*Acantholimon* sp.	Plumbaginaceae
84(2)	1320	aboundent	twig & foliage	7.1	Shrub	*L. vesicarium L.*	Brassicaceae
84(3)	1320	aboundent	twig & foliage	7.1	Shrub	Unknownable	Chenopodiaceae
84(4)	1320	partly aboundent	twig & foliage	7.1	Shrub	*Pteropyrum* sp.	Polygonaceae
84(5)	1320	aboundent	twig & foliage	7.1	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae
84(6)	1320	outspread	twig & foliage	7.1	Shrub	*A. odontostephana* Boiss.	Asteraceae
84(7)	1320	partly aboundent	twig & foliage	7.1	Shrub	*Salvia* sp.	Lamiaceae
84(8)	1320	partly aboundent	twig & foliage	7.1	Shrub	*Dorema* sp.	Apiaceae
84(9)	1320	aboundent	twig & foliage	7.1	Shrub	*Artemisia* sp.	Asteraceae
84(10)	1320	aboundent	twig & foliage	7.1	Shrub	*E.* c.f. *myrsinites* L.	Euphorbiaceae
85	1198	aboundent	twig & foliage	7.8	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae
86	1171	aboundent	twig & foliage	7.1	Shrub	Unknownable	Chenopodiaceae
87(1)	1331	aboundent	twig & foliage	7.4	Shrub	*L. vesicarium L.*	Brassicaceae
87(2)	1331	aboundent	twig & foliage	7.4	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae
87(3)	1331	aboundent	twig & foliage	7.4	Shrub	Unknownable	Chenopodiaceae
87(4)	1331	partly aboundent	twig & foliage	7.4	Shrub	*Pteropyrum* sp.	Polygonaceae
67(1)	1184	aboundent	twig & foliage	7.1	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae
67(2)	1184	aboundent	twig & foliage	7.1	Shrub	Unknownable	Chenopodiaceae
67(3)	1184	aboundent	twig & foliage	7.1	Shrub	*Artemisia* sp.	Asteraceae
67(4)	1184	aboundent	twig & foliage	7.1	Shrub	*N. meyeri* Benth.	Lamiaceae
67(5)	1184	aboundent	twig & foliage	7.1	Shrub	*L. vesicarium L.*	Brassicaceae
49(1)	1236	aboundent	twig & foliage	7.7	Shrub	*Artemisia* sp.	Asteraceae
49(2)	1236	aboundent	twig & foliage	7.7	Shrub	Unknownable	Chenopodiaceae
49(3)	1236	aboundent	twig & foliage	7.7	Shrub	*Acantholimon* sp.	Plumbaginaceae
49(4)	1236	aboundent	twig & foliage	7.7	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae
49(5)	1236	aboundent	twig & foliage	7.7	Shrub	Unknownable	Unknownable
22(1)	1215	aboundent	twig & foliage	7.7	Shrub	*S. inflata* Benth.	Lamiaceae
22(2)	1215	aboundent	twig & foliage	7.7	Shrub	*Acantholimon* sp.	Plumbaginaceae
22(3)	1215	aboundent	twig & foliage	7.7	Shrub	*S. inflata* Benth.	Lamiaceae
22(4)	1215	aboundent	twig & foliage	7.7	Shrub	*E. myrsinites* L.	Euphorbiaceae

Table 3. Cont.

22(5)	1215	aboundent	twig & foliage	7.7	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae
24(1)	928	partly aboundent	twig & foliage	7.1	Shrub	Unknownable	Chenopodiaceae
24(2)	928	partly aboundent	twig & foliage	7.1	Shrub	*Artemisia* sp.	Asteraceae
24(3)	928	partly aboundent	twig & foliage	7.1	Shrub	*Pteropyrum* sp.	Polygonaceae
24(4)	928	aboundent	twig & foliage	7.1	Shrub	*T. stocksiana* (Boiss.) Drude	Apiaceae
26(1)	850	aboundent	twig & foliage	7.7	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae
26(2)	850	aboundent	twig & foliage	7.7	Shrub	Unknownable	Chenopodiaceae
53(1)	922	aboundent	twig & foliage	7.6	Shrub	*Pteropyrum* sp.	Polygonaceae
53(2)	922	partly aboundent	twig & foliage	7.6	perennial herb	*B. multifida* DC.	Geraniaceae
53(3)	922	partly aboundent	twig & foliage	7.6	Shrub	*S. glaucus* L.	Asteraceae
53(4)	922	partly aboundent	twig & foliage	7.6	Shrub	*A. odontostephana* Boiss.	Asteraceae
51(1)	940	intermediate	twig & foliage	7	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae
51(2)	940	intermediate	twig & foliage	7	Shrub	*Artemisia* sp.	Asteraceae
51(3)	940	intermediate	twig & foliage	7	Shrub	Unknownable	Chenopodiaceae
51(4)	940	intermediate	twig & foliage	7	Shrub	Unknownable	Rubiaceae
51(5)	940	intermediate	twig & foliage	7	Shrub	*A. odontostephana* Boiss.	Asteraceae
51(6)	940	intermediate	twig & foliage	7	Shrub	*T. stocksiana* (Boiss.) Drude	Apiaceae
51(7)	940	intermediate	twig & foliage	7	Shrub	*N. meyeri* Benth.	Lamiaceae
69(1)	854	aboundent in alteration wall	twig & foliage	7.7	Shrub	*L. vesicarium L.*	Brassicaceae
69(2)	854	aboundent	twig & foliage	7.7	Shrub	*A. odontostephana* Boiss.	Asteraceae
69(3)	854	aboundent	twig & foliage	7.7	Shrub	*T. stocksiana* (Boiss.) Drude	Apiaceae
69(4)	854	aboundent	twig & foliage	7.7	Shrub	*Acantholimon* sp.	Plumbaginaceae
97(1)	843	partly aboundent	twig & foliage	7.8	Shrub	*P. harmala L.*	Zygophyllaceae
97(2)	843	partly aboundent	twig & foliage	7.8	Shrub	Unknownable	Rubiaceae
97(3)	843	partly aboundent	twig & foliage	7.8	Shrub	Unknownable	Chenopodiaceae
91(1)	835	outspread	twig & foliage	7.1	Shrub	Unknownable	Apiaceae
91(2)	835	outspread	twig & foliage	7.1	Shrub	*S. inflata* Benth.	Lamiaceae
91(3)	835	outspread	twig & foliage	7.1	Shrub	*Salvia* sp.	Lamiaceae
71(1)	881	outspread	twig & foliage	7.1	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae
71(2)	881	outspread	twig & foliage	7.1	Shrub	*Artemisia* sp.	Asteraceae
71(3)	881	outspread	twig & foliage	7.1	Shrub	*Pteropyrum* sp.	Polygonaceae

Table 3. Cont.

71(4)	881	outspread	twig & foliage	7.1	Shrub	*A. odontostephana* Boiss.	Asteraceae
89(1)	815	aboundent	twig & foliage	7.2	Shrub	*Pteropyrum* sp.	Polygonaceae
89(2)	815	aboundent	twig & foliage	7.2	Shrub	Unknownable	Chenopodiaceae
89(3)	815	aboundent	twig & foliage	7.2	Shrub	*L. vesicarium L.*	Brassicaceae
164(1)	720	aboundent	twig & foliage	7.7	Shrub	Unknownable	Unknownable
164(2)	720	outspread	twig & foliage	7.7	Shrub	*Tragopogon* sp.	Asteraceae
164(3)	720	aboundent	twig & foliage	7.7	Shrub	*Crepis* sp.	Asteraceae
164(4)	720	partly aboundent	twig & foliage	7.7	Shrub	*N. meyeri* Benth.	Lamiaceae
164(5)	720	partly aboundent	twig & foliage	7.7	Shrub	*S. glaucus* L.	Asteraceae
164(6)	720	partly aboundent	twig & foliage	7.7	Shrub	*T. stocksiana* (Boiss.) Drude	Apiaceae
182(1)	715	aboundent	twig & foliage	7.8	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae
182(2)	715	aboundent	twig & foliage	7.8	Shrub	*Artemisia* sp.	Asteraceae
182(3)	715	aboundent	twig & foliage	7.8	Shrub	Unknownable	Unknownable
208(1)	710	aboundent	twig & foliage	7.5	Shrub	Unknownable	Chenopodiaceae
208(2)	710	aboundent	twig & foliage	7.5	Shrub	*Artemisia* sp.	Asteraceae
208(3)	710	aboundent	twig & foliage	7.5	Shrub	Unknownable	Unknownable
172(1)	747	partly aboundent	twig & foliage	7.8	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae
172(2)	747	partly aboundent	twig & foliage	7.8	Shrub	Unknownable	Rubiaceae
172(3)	747	partly aboundent	twig & foliage	7.8	Shrub	*Acantholimon* sp.	Plumbaginaceae
172(4)	747	partly aboundent	twig & foliage	7.8	Shrub	*L. depressum* Stocks	Solanaceae
172(5)	747	partly aboundent	twig & foliage	7.8	Shrub	Unknownable	Chenopodiaceae
166(1)	732	aboundent	twig & foliage	7.5	Shrub	*Artemisia* sp.	Asteraceae
166(2)	732	aboundent	twig & foliage	7.5	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae
166(3)	732	aboundent	twig & foliage	7.5	Shrub	*Crepis* sp.	Asteraceae
166(4)	732	aboundent	twig & foliage	7.5	Shrub	Unknownable	Unknownable
166(5)	732	outspread	twig & foliage	7.5	Shrub	*Cruciata* sp.	Rubiaceae
200(1)	706	aboundent	twig & foliage	7.6	Shrub	*Cousinia* sp.	Asteraceae
200(2)	706	aboundent	twig & foliage	7.6	Shrub	*E. myrsinites* L.	Euphorbiaceae
200(3)	706	aboundent	twig & foliage	7.6	Shrub	*Astragalus (sect. Onobrychioidei)*	Fabaceae
200(4)	706	aboundent	twig & foliage	7.6	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae
204(1)	695	aboundent	twig & foliage	7.6	Shrub	*Astragalus (sect. Onobrychioidei)*	Fabaceae
204(2)	695	aboundent	twig & foliage	7.6	Shrub	*Cousinia* sp.	Asteraceae

Table 3. Cont.

204(3)	695	partly aboundent	twig & foliage	7.6	Shrub	*Artemisia* sp.	Asteraceae
216(1)	693	aboundent	twig & foliage	7.7	Shrub	Unknownable	Chenopodiaceae
216(2)	693	aboundent	twig & foliage	7.7	Shrub	Unknownable	Unknownable
213(1)	684	aboundent	twig & foliage	7.7	perennial herb	Unknownable	Unknownable
213(2)	684	aboundent	twig & foliage	7.7	Shrub	*Artemisia* sp.	Asteraceae
194(1)	668	aboundent	twig & foliage	7.6	Shrub	Unknownable	Chenopodiaceae
194(3)	668	aboundent	twig & foliage	7.6	Shrub	*P. harmala L.*	Zygophyllaceae
194(4)	668	outspread	twig & foliage	7.6	Shrub	*A.* (sect. *Scorodon*) *umbilicatum* Boiss.	Alliaceae
194(5)	668	partly aboundent	twig & foliage	7.6	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae
238(1)	685	aboundent	twig & foliage	7.1	Shrub	Unknownable	Unknownable
238(2)	685	partly aboundent	twig & foliage	7.1	Shrub	*Salvia* sp.	Lamiaceae
238(3)	685	outspread	twig & foliage	7.1	Shrub	*Astragalus* (sect. Onobrychioidei)	Fabaceae
238(4)	685	outspread	twig & foliage	7.1	Shrub	*M. coerulea* (Willd.) Lehm.	Boraginaceae
238(5)	685	aboundent	twig & foliage	7.1	Shrub	Unknownable	Chenopodiaceae
238(6)	685	outspread	twig & foliage	7.1	Shrub	*A. pseudoalhaji* (M. Bieb.) Decv.	Fabaceae
238(7)	685	outspread	twig & foliage		Shrub	*P. harmala L.*	Zygophyllaceae
247(1)	700	aboundent	twig & foliage	7.7	Shrub	Unknownable	Unknownable
247(2)	700	aboundent	twig & foliage	7.7	perennial herb	*Acantholimon* sp.	Plumbaginaceae
247(3)	700	partly aboundent	twig & foliage	7.7	Shrub	*P. harmala L.*	Zygophyllaceae
247(4)	700	partly aboundent	twig & foliage	7.7	Shrub	*Astragalus* (sect. Onobrychioidei)	Fabaceae
188(1)	717	partly aboundent	twig & foliage	7.7	Shrub	*Artemisia* sp.	Asteraceae
188(2)	717	partly aboundent	twig & foliage	7.7	Shrub	Unknownable	Chenopodiaceae
188(3)	717	outspread	twig & foliage	7.7	Shrub	*Crepis* sp.	Asteraceae
252(1)	724	partly aboundent	twig & foliage	7.7	Shrub	*Artemisia* sp.	Asteraceae
252(2)	724	partly aboundent	twig & foliage	7.7	Shrub	Unknownable	Unknownable
260(1)	704	partly aboundent	twig & foliage	7.1	Shrub	*L. vesicarium L.*	Brassicaceae
260(2)	704	aboundent	twig & foliage	7.1	Shrub	Unknownable	Rubiaceae
260(3)	704	aboundent	twig & foliage	7.1	Shrub	*Artemisia* sp.	Asteraceae
260(4)	704	aboundent	twig & foliage	7.1	Shrub	*A. odontostephana* Boiss.	Asteraceae
260(5)	704	aboundent	twig & foliage	7.1	Shrub	*S. sulphureum* (Banks & Soland.) Bornm.	Brassicaceae

Table 4. Summary statistic parameters for soil and plant samples and their BACs in the study area

Element	Au			Ag			As			Cu			Hg			Mo		
Analyze method	ME-VEG41	Au-ICP21		ME-VEG41	ME-MS41		ME-VEG41	ME-MS41		ME-VEG41	ME-MS41		ME-VEG41	ME-MS41		ME-VEG41	ME-MS41	
Unit	**Ppm**	**ppm**		**ppm**	**ppm**		**ppm**	**ppm**		**ppm**	**ppm**		**ppm**	**ppm**		**ppm**	**ppm**	
Medium	*Plant*	*soil*	*BAC*	*plant*	*soil*	*BAC*	*plant*	*soil*	*BAC*	*plant*	*soil*	*BAC*	*plant*	*soil*	*BAC*	*plant*	*soil*	*BAC*
Lower limit	0.0002	0.001		0.002	0.01		0.1	0.1		0.01	0.2		0.001	0.01		0.01	0.05	
Upper limit	100	10		100	100		10000	10000		10000	10000		100	10000		10000	10000	
Max.	0.03	0.30	1.15	0.32	3.28	0.99	45.60	829	0.67	77	2660	1.10	0.07	6.10	1.15	18.4	43.2	6.50
Min.	0.00	0.00	0.00	0.00	0.05	0.00	0.30	9	0.00	4.22	13.4	0.00	0.00	0.02	0.00	0.31	1.07	0.05
Mean	0.00	0.06	0.11	0.03	0.54	0.11	3.32	106.52	0.06	13.07	262.79	0.15	0.01	0.29	0.26	1.66	8.15	0.31
Median	0.00	0.02	0.05	0.02	0.25	0.05	1.70	48.90	0.03	10.45	116	0.09	0.01	0.05	0.18	0.96	4.67	0.19
St dv	0.00	0.08	0.19	0.04	0.66	0.17	5.84	160.25	0.09	9.04	449.31	0.18	0.01	1.10	0.23	2.48	9.50	0.61
Variance	0.00	0.01	0.04	0.00	0.43	0.03	34.15	25680	0.01	81.65	201879	0.03	0.00	1.20	0.05	6.14	90.23	0.37

Geraniaceae, Lamiaceae, Plumbaginaceae, Polygonaceae, Rubiaceae, Solanaceae and Zygophyllaceae. List of plant samples with their botanical identification is brought in Table 3.

As shown in Figure 2, Astearceae is the most abundant family in the samples. After that Brassicaceae ‹Chenopodiaceae ‹Lamiaceae ‹Apiaceae, Plumbaginaceae are abundant in the area. Summary statistic parameters for soil and plant samples and their BACs in study area are brought in Table 4.

Arsenic (As)

Most samples with high contents of "As" in study area belong to *Artemisia* sp. (45.6ppm, pH=7.1). BAC means of "As" for *S. inflata*, *Salvia* sp., *Artemisia* sp. and *Astragalus* sp. are 0.48, 0.12, 0.11, and 0.10, respectively (Table 3). Based on Perel'man's classification, "As" in *S. inflata*, *Salvia* sp., and *Artemisia* sp. shows intermediate absorption and in *Astragalus* sp. shows weak absorption. The studied plants *S. inflata*, *Salvia* sp. and *Artemisia* sp. which are widely distributed in the studied area could be as arsenic indicator in the study area.

Arsenic is famous for its toxicity. Although "As" is an essential element for the metabolism of carbohydrates in fungi and algae (Adriano, 1992), plants can still accumulate certain amount of this element without exhibiting any visible harmful effects (Burlo et al., 1999).

Mercury (Hg)

The highest contents of "Hg" are 0.07, 0.04 ppm (Table 4) that belong to *Artemisia* sp. and *Crepis* sp. For only *S. inflata* (1.05) BAC mean exceeds "hyperaccumulation" definition criterion value of BAC>1.0 for "Hg". Mean BACs for *Salvia* sp. (0.53), *M. coerulea* (0.45), *P. harmala* (0.44) and *Artemisia* sp. (0.34) are higher than others.

Based on Perel'man classification (Table 2),"Hg" shows strong absorption in *S. inflata* and intermediate absorption in *Salvia* sp., *M. coerulea*, *P. harmala* and *Artemisia* sp.

Table 5. Mean biological absorption coefficients (BAC) for soil -plant in this study for different mediums

Scientific name	***Family***	***Au***	***Ag***	***As***	***Cu***	***Hg***	***Mo***	***Re***	***Sb***	***Te***
S. inflate	Lamiaceae	0.33	0.71	0.48	1.10	1.05	0.73	4.4	0.38	0.36
Salvia sp.	Lamiaceae	0.20	0.23	0.12	0.46	0.53	0.62	18.7	0.18	0.07
Artemisia sp.	Asteraceae	0.20	0.17	0.11	0.19	0.34	0.23	96.7	0.15	0.12
Acantholimon sp.	Plumbaginaceae	0.10	0.15	0.08	0.15	0.33	0.19	2.9	0.14	0.08
M. coerulea	Boraginaceae	0.17	0.16	0.04	0.78	0.45	0.59	116.0	0.12	0.02
B. multifida	Geraniaceae	0.08	0.05	0.04	0.05	0.30	0.24	40.5	0.10	0.05
Pteropyrum sp.	Polygonaceae	0.15	0.17	0.04	0.12	0.29	0.21	10.7	0.08	0.07
P. harmala	Zygophyllaceae	0.08	0.16	0.04	0.16	0.44	0.28	75.6	0.08	0.04
Astragalus sp.	Fabaceae	0.36	0.10	0.10	0.21	0.21	1.92	52.9	0.07	0.12
Unknownable	Chenopodiaceae	0.09	0.09	0.04	0.10	0.17	0.35	108.2	0.06	0.06
A. pseudoalhaji	Fabaceae	0.17	0.10	0.02	0.34	0.02	0.11	5.3	0.06	0.02
E. myrsinites	Euphorbiaceae	0.03	0.05	0.03	0.10	0.26	0.11	20.4	0.06	0.07
S. sulphureum	Brassicaceae	0.06	0.05	0.04	0.11	0.22	0.20	91.6	0.05	0.05
Allium sp.	Alliaceae	0.05	0.04	0.01	0.09	0.30	0.14	52.0	0.05	0.02
L. vesicarium	Brassicaceae	0.03	0.06	0.02	0.11	0.18	0.36	90.0	0.05	0.04
Unknownable	Rubiaceae	0.04	0.03	0.02	0.05	0.20	0.10	78.3	0.04	0.06
Cousinia sp.	Asteraceae	0.19	0.10	0.04	0.11	0.14	0.18	15.3	0.04	0.21
Cruciata sp.	Rubiaceae	0.13	0.01	0.03	0.07	0.12	0.16	14.0	0.04	0.02
S. glaucus	Asteraceae	0.03	0.02	0.02	0.04	0.13	0.27	51.0	0.03	0.02
N. meyeri	Lamiaceae	0.01	0.03	0.02	0.02	0.23	0.13	592.8	0.02	0.07
Crepis sp.	Asteraceae	0.05	0.02	0.02	0.07	0.13	0.17	40.1	0.02	0.06
Tragopogon sp.	Asteraceae	0.01	0.01	0.01	0.03	0.13	0.16	40.0	0.01	0.02
L. depressum Stocks	Solanaceae	0.05	0.05	0.02	0.06	0.19	0.21	3.0	0.01	0.11
T. stocksiana	Apiaceae	0.01	0.02	0.01	0.04	0.13	0.12	426.8	0.01	0.12

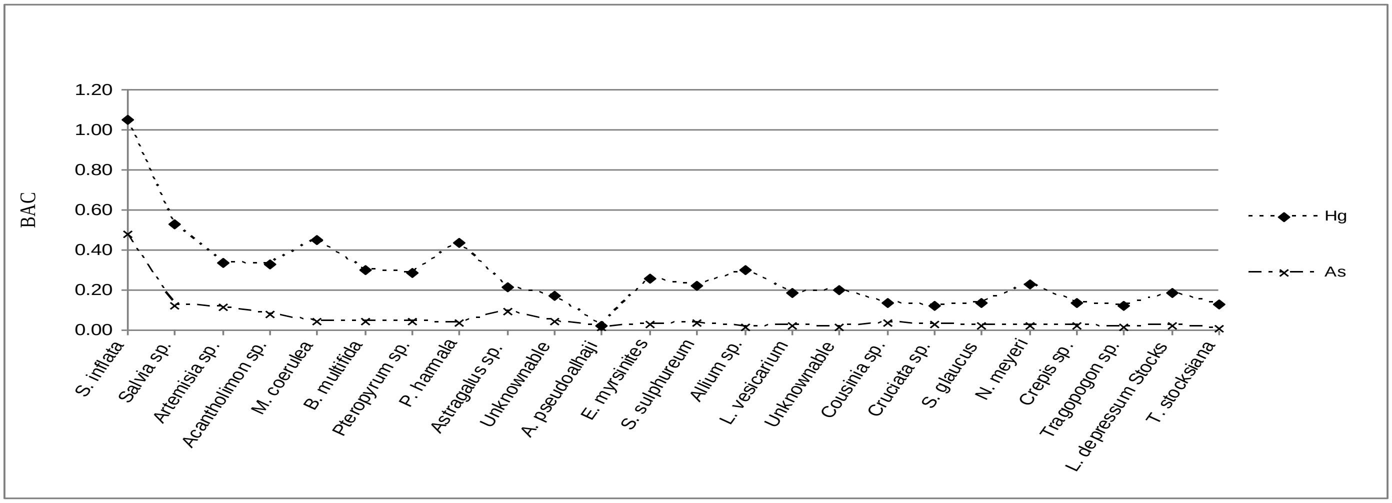

Figure 3. Comparing of BAC mean values of As, Hg for sampled plants in study area

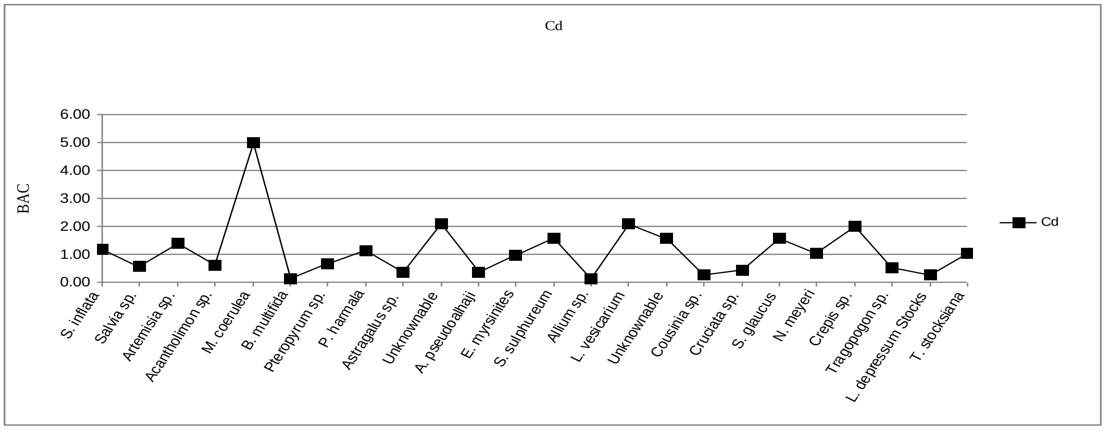

Figure 4. Comparing of BAC mean values of Cd for sampled plants in study area

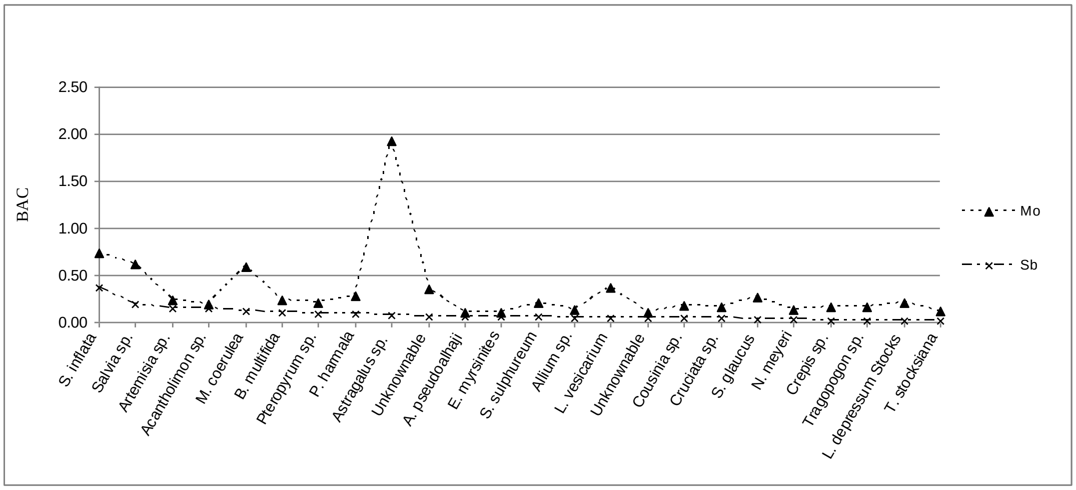

Figure 5. Comparing of BAC mean values of Mo, Sb for sampled plants in study area

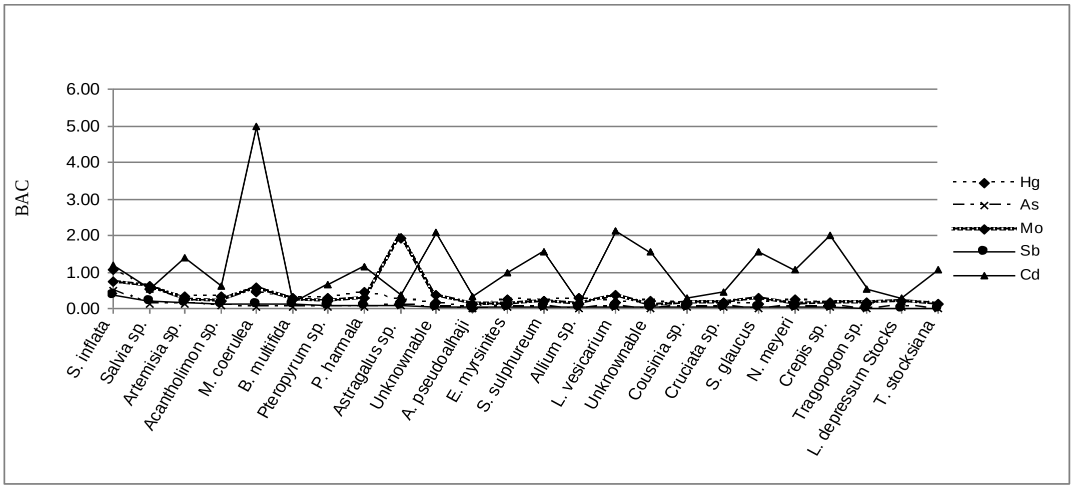

Figure 6. Comparing of BAC mean values of Mo, Sb for sampled plants in study area

Table 6. Hyperaccumulators and indicators for different mediums in this study

Plant	Hyperaccumulator	Indicator
S. inflata	Cd, Hg	As, Mo, Sb
Chenopodiaceae	Cd	-
S. sulphureum	Cd	-
L. vesicarium	Cd	-
Artemisia sp.	Cd	As, Hg, Sb
Crepis sp.	Cd	-
S. glaucus	Cd	-
Rubiaceae	Cd	-
Astragalus sp.	Mo	-
N. meyeri	Cd	-
Salvia sp.	-	As, Hg, Mo, Sb
P. harmala	Cd	Hg
T. stocksiana	Cd	-
M. coerulea	-	Hg, Mo

S. inflata is locally abundant and have mean BAC>1, then it can be a hyperaccumulator of Hg. The studied plants *Salvia* sp., *M. coerulea, P. harmala* and *Artemisia* sp. which were widely distributed in Masjed-Daghi could be as Hg indicator in the study area.

Cadmium (Cd)

Because Cadmium background value of plants in the studied area is high, all of the identified plants have moderate values of mean absorption. Cadmium is not known to be an essential element for plant metabolism, and then considerable amount of it has been undertaken on uptake of Zn by plants, and its movement within plants (Dunn, 2007). *Moltkia coerulea*, *Lepidium vesicarium*, *Stachys inflata*, Peganum harmala, *Nepeta meyeri*, *Torilis stocksiana*, Sterigmostemum sp., *Senecio glaucus*, *Crepis* sp., *Artemisia* sp., Chenopodiaceae, and Rubiaceae introduce as hyperaccumulators of cadmium.

Molybdenum (Mo)

Highest values of "Mo" are found in *Astragalus* sp. (18.4 ppm) and *S. glaucus* (16.7ppm). Mean BAC are for *Astragalus* sp. 1.92, this is average of BACs. Meanwhile, maximum value for BAC for this species is found 6.5, *S. inflata* (0.73), *Salvia* sp. (0.62) and M. coerulea (0.59; Table 3).

Based on Perel’man classification (table2), *Astragalus* sp. shows strong absorption and the others show intermediate absorption of molybdenum in the study area. *Astragalus* sp. with a local abundance and mean BAC>1 introduces as "Cu" hyperaccumulator and *S. inflata*, *Salvia* sp., and *M. coerulea* with intermediate absorption (BAC>0.5) are widely distributed in Masjed-Daghi area and useful as molybdenum indicators throughout the area.

Antimony (Sb)

Among other toxic elements, antimony (Sb) is one of the least studied. Sb is a potentially toxic element with unknown biological function and as a matter of fact Sb is more toxic to plants than was expected from previous (Shtangeeva et al., 2010).The highest concentration of Sb is found in *Artemisia* sp. (1.78 ppm). BAC mean evaluated for *S. inflata*, *Salvia* sp., *Artemisia* sp., *Acantholimon* sp .and *M. coerulea* are 0.38, 0.18, 0.15, 0.14, and 0.12, respectively. Antimony absorptions in in above plants are intermediate absorption (table 2) *S. inflata*, *Salvia* sp. and *Artemisia* sp. with good abundance could be used as Sb indicators.

CONCLUSION

All studied plants are native and widely distributed in Masjed-Daghi area. Biogeochemical functions of these plants are also extraordinary as they accumulate Hg, Mo, and Ag by BAC averagely up to 1.05. Meanwhile, in this study it has been demonstrated that using the biogeochemical technique may assist in distinguishing regionally contaminated areas. The metal hyper accumulation abilities for (Hg, Cd) of *S. inflata* and (Cd) of Chenopodiaceae could be useful for phytodermiation (Figure 6) because they are native and widely distributed in study area and accumulate metals several times more than soil metal contents.

S. inflata can be especially useful for indicating of (Cd, Hg, As, Mo, Sb), *Artemisia* sp. for (Cd, As, Hg, Sb), *M. coerulea* for (Hg, Mo), and *Salvia* sp. for (As, Hg, Mo, Sb) mineral contents (Table 6) in the northwest of Iran.

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