

# Potentially toxic elements in the soil and two indigenous plant species in Dashkasan epithermal gold mining area, West Iran

Farid Moore<sup>1</sup> · Reza Dehbandi<sup>1</sup> · Behnam Keshavarzi<sup>1</sup> · Keyvan Amjadian<sup>2</sup>

Received: 6 January 2015 / Accepted: 21 September 2015  
© Springer-Verlag Berlin Heidelberg 2015

**Abstract** Concentrations and environmental indices of 18 elements (Al, Ag, As, Au, Bi, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, S, Sb, U, and Zn) in 15 top soil samples (0–20 cm) at Dashkasan epithermal gold mining area, Kurdistan Province, Iran indicated high Ag, Au, As, Hg, Sb and Pb pollution reflecting natural mineralization and mining activity. Also the leaves of two indigenous medicinal plant species, *Ephedra major* subsp. *procera* and *Achillea aleppica*, were sampled and analyzed. The results demonstrated that the mean concentration of Au, Cd, and Sb in *Ephedra* and *Achillea* is higher than the averages in natural plants in other parts of the world. Calculated biological concentration factors (BCF) revealed that *Ephedra* species is a cadmium accumulator, while *Achillea* efficiently accumulates cadmium and molybdenum. High metals affinity for sulfur in soil, low BCF values and relatively low total metals content in plants confirmed that most chalcophile metals in the analyzed plant species exhibit low bioavailability and hence pose no immediate health risk. However, continuous consumption of *Ephedra* and *Achillea* is a potential health threat to livestock and local population.

**Keywords** Dashkasan mine · Toxic elements · Soil · Plant

## Introduction

Mining is a major source of environmental trace element contamination with serious negative impacts on the environment and ecosystem (Razo et al. 2004; Chopin and Alloway 2007; Navarro et al. 2008). Generally, in the vicinity of mines and ore dressing plants, elements are unlocked from the host minerals by extraction and beneficiation processes like crushing, grinding, leaching and smelting. Natural weathering processes also accelerate by mining activities (Adriano 1986; Getaneh and Alemayehu 2006).

Potentially toxic elements in open and partially covered mine dumps and tailing basins are usually scattered in the surrounding environment. Therefore, elevated metal levels commonly occur in the adjacent agricultural soils, food crops, and drainage systems (Martínez-Sánchez et al. 2009).

Some elements are nonessential and deleterious, indicating that even at low concentrations; they are toxic to both plants and their consumers (Alloway 1990). However, at low concentrations, some other trace elements (e.g., Fe, Mn, B, Cu, Cr, Mo, Ni, Se and Zn) are essential for healthy functioning of plants (Alloway 1990; McBride 1994).

A huge difference in metal uptake between plant species is already demonstrated in many studies (Archer and Caldwell 2004; Chopin and Alloway 2007). Moreover, some plants reveal a special capability in accumulating a specific element.

Plants are also intermediate reservoirs through which trace elements from soils, and partly from water and air, move to man and animals (Kabata-Pendias 2011). Hence contamination of soils by potentially toxic elements is a primary concern in the mining sites because of their toxicity, persistence, and accumulation in food chains (Donkor et al. 2005).

✉ Reza Dehbandi  
rezadehbandi65@gmail.com

<sup>1</sup> Department of Earth Sciences, College of Sciences, Shiraz University, Shiraz 71454, Iran

<sup>2</sup> Department of Petroleum Geosciences, Faculty of Science, Soran University, Delizian, Soran/Erbil, Kurdistan Regional Government, Iraq

Previous published work concerning Dashkasan mine are limited (e.g., Boccaletti et al. 1976; Bolourchi 1979; Rastad et al. 2000; Wilkinson and Bartran 2003; Richards et al. 2006); environmental assessments are even more scarce (Sayyareh et al. 2005; Rafiei 2010). The present study focuses on Dashkasan gold and antimony mining area, in northwest Iran. Mining operation in Dashkasan began around 70 years ago and despite several temporarily cessation of mining activity, it remained to be a potential source of trace element contamination in the area. This work mostly deals with the evaluation of possible adverse effects of 18 major and trace elements (Ag, Al, As, Au, Bi, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, S, Sb, U and Zn) on the quality of soil and two endemic natural plant species in the study area.

## Geological setting

Dashkasan also known as Sari Gunay is the largest known epithermal gold deposit in Iran (Niroomand et al. 2013). With 20 km<sup>2</sup> surface area, it is located within a latitic to trachytic volcanic complex, 42 km of Qorveh City in Kurdistan province. The geographic coordinates are 35°10'03"–35°14'30"N and 48°01'38"–48°07'38"E. The origin of the ore deposit is still a matter of debate. Richards et al. (2006) argued that Dashkasan gold deposit must be regarded as a gold-rich porphyry and epithermal Au deposit associated with high-K calc-alkaline to shoshonitic magmas. However, Niroomand et al. (2013) suggested that Dashkasan is a low sulfidation type epithermal gold deposit.

Stocklin (1968) on the basis of occurrence and distribution of gold deposits and indications has divided Sanandaj-Sirjan magmatic-metamorphic zone into two northern (Golpayegan–Naghadeh–Makoo) and southern (Golpayegan–Sirjan) parts, with the northern part being richer in gold. The study area (Fig. 1) is located in the northern sector. Although Dashkasan mine has a history of Arsenic and antimony mining, nowadays it is mostly sought for gold.

The outcropped rocks are Jurassic to Quaternary in age (Richards et al. 2006) (Fig. 1). The plutonic rocks in the area principally comprise alkaline microgranitoids with microgranular porphyritic textures. The width and length of the mineralized veins in Dashkasan mine vary from 3 to 30 cm and 100 to 1000 m, respectively. Gold mineralization mostly occurred in the waning stages of an epithermal-style quartz-pyrite-stibnite-realgar-orpiment veining (Richards et al. 2006; Niroomand et al. 2013).

The veins are hosted by subvolcanic rocks. The resulting wall-rock alteration is mostly silicic, chloritic, sericitic,

pyritic and argillic (Rastad et al. 2000; Richards et al. 2006; Niroomand et al. 2013).

Gold mining in Dashkasan involves both open-pit and underground operations. There is no smelter and the waste rocks are dumped as heap tailings. Exploration drilling revealed that the deposit contained 52 million metric tons (Mt) of oxide mineralization grading 1.77 g/t Au in an area of 0.72 km<sup>2</sup> and to a depth of 350 m (Wilkinson and Bartran 2003). Important associated elements are Sb + Hg ± As ± (Pb ± Zn) (Ghorbani 2013).

Mining has produced huge quantity of waste, among which are fine-grained ore minerals including arsenopyrite, and weathering products (Fe-oxyhydroxides, sulfates and scorodite) (Lescuyer et al. 2003). According to Kurdistan Meteorological Office report (2013), mean annual precipitation is 350 mm mostly in the form of snow. The lowest and highest average annual temperatures are −0.5 and 25.5 °C, respectively.

## Materials and methods

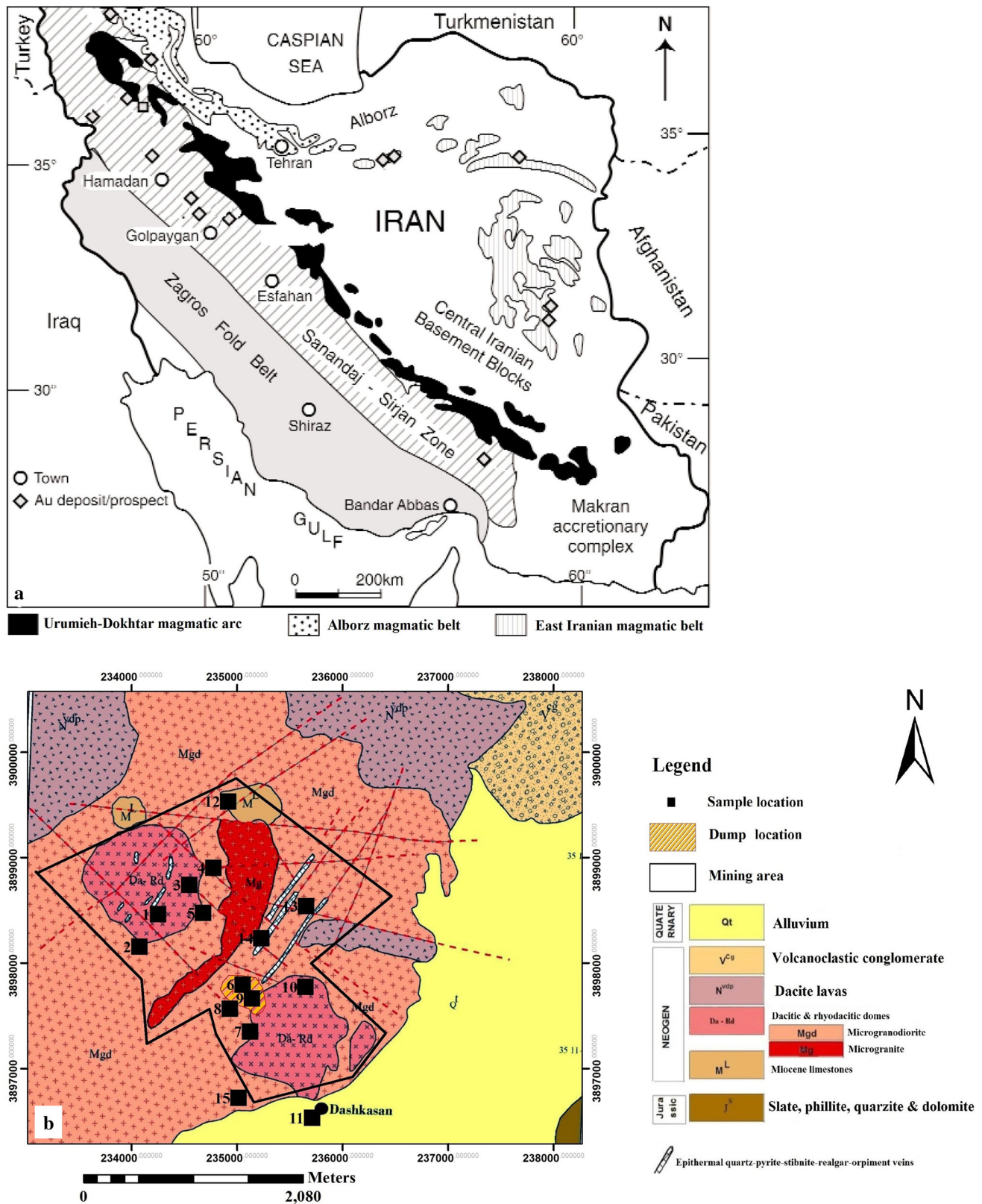
Composite top soil samples (0–20 cm) were collected at 15 locations (Fig. 1). A control sample (No. 16) was also collected approximately 2 km from the mine quarry.

The soil samples were air dried at room temperature (about 25 °C) for 2 weeks and then passed through a 0.063 mm polyethylene sieve to remove plant debris, pebbles and stones.

Soil texture was determined by hydrometry and sieve analysis (Bowles 1992). Soil classification was carried out using Folks (1980) classification system. Once the organic matter was removed, the remaining mineral sample was weighted and subjected to particle size analysis to determine sand (2–0.0625 mm), silt (0.0625–0.002 mm) and clay (<0.002 mm) fractions. The samples were dried for 2 days at 60 °C. The dried soil samples were disaggregated, sieved on a 10 mesh (2 mm) screen, then quartered, pulverized and passed through a 120 mesh (<125 µm) sieve.

Soil pH was measured in water with a 1:2.5 soil/solution ratio after equilibrium for 30 min. For soil digestion, nominally 0.2 g of each dry sample was mixed with concentrated hydrochloric (HCl) and nitric (HNO<sub>3</sub>) acids and sealed within a digestion vessel. The vessel was then placed into a microwave digestion machine and heated to 160–170 °C using microwave energy. After digestion, distilled water was added to dilute the acid solution and samples were poured into test tubes.

Soil samples were analyzed for their major and trace element contents in accredited Acme Analytical Laboratories, Vancouver, B.C, Canada using inductively coupled plasma mass spectrometry (ICP-MS).



**Fig. 1** **a** Main tectonic zones and Mesozoic–Cenozoic magmatic belts of Iran (after Alavi et al. 1997; Stocklin 1968) displaying gold occurrences, prospects, and mines in Iran (modified after Moritz et al.

2006); **b** geological map showing soil sampling locations at Dashkasan deposit

Repetitive and control samples were used to assess the precision and accuracy, respectively.

To investigate elemental associations among the analyzed elements in soil, the normality of the data was checked using one sample Shapiro–Wilks test. The results show that all parameters in Dashkasan mine are non-normally distributed in soil samples (significant level 0.05). Hence, a Spearman rank correlation analysis was applied to all soil samples using Statistical Package for Social Science (SPSS v. 19).

The assessment of soil elemental enrichment was carried out by calculating the enrichment factor (EF) (Loska et al. 2003). EF is the relative abundance of a chemical element in soil compared to the reference environment (Buat-Mernard 1979; Hernandez et al. 2003; Loska et al. 2003; Pekey 2006):

$$EF = (C_n/C_{ref})/(B_n/B_{ref})$$

where EF is the enrichment factor,  $C_n$  and  $B_n$  are average element concentration in samples and reference environment, respectively.  $C_{ref}$  and  $B_{ref}$  are the average concentration of the reference element in soil samples and reference environment, respectively (Loska et al. 2003; Pekey 2006). The most common reference elements in environmental studies are Al, Fe, Si, Ti, Sc, Y, Sc, and Mn (Eby 2004; Zhang et al. 2007a). In the present study Al was used as the reference element since it displays low occurrence variability and is a major component of the Earth's crust. The reference environment adopted in this study is the concentrations of elements in soil control sample (No. 16). Five contamination categories are commonly recognized on the basis of Enrichment Factor as suggested by Chen et al. (2007) (Table 1).

Contamination factor was also calculated to assess the soil contamination using the following formula:

$$C_f^i = \frac{C_0^i - 1}{C_n^i}$$

where  $C_0^i - 1$  is the mean metal content at sampling sites and  $C_n^i$  is the concentration of elements in Earth's crust as a

**Table 1** Categories of enrichment factor (Chen et al. 2007)

EF range	Enrichment grade	Enrichment level
$EF < 1$	1	Without enrichment
$1 \leq EF < 3$	2	Deficiency to minimal enrichment
$3 \leq EF < 5$	3	Moderate enrichment
$5 \leq EF < 10$	4	Moderate to high enrichment
$10 \leq EF < 25$	5	High enrichment
$25 \leq EF < 50$	6	Very high enrichment
$50 \leq EF$	7	Extremely high enrichment

**Table 2** Categories of contamination factor (Hakanson 1980)

CCF range	Contamination level
$CF < 1$	Deficiency to minimal contamination
$1 \leq CF < 3$	Moderate contamination
$3 \leq CF < 6$	Considerable contamination
$6 \leq CF$	Extremely high contamination

reference value. Four contamination categories are distinguished as suggested by Hakanson (1980) (Table 2). Concentration in local background sample was regarded as the reference value.

The pollution load index in different samples was also calculated using the following formula:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times \dots \times CF_n}$$

where PLI is the pollution load index, CFs are the contamination factors and n is the number of elements. The PLI value  $> 1$  indicates polluted soil, whereas  $< 1$  indicates no pollution (Tomlinson et al. 1980).

Major shrub plants genera in the vicinity of Dashkasan mine are *Ephedra major* subsp. *procera* (C.A. Mey.) Bornm. (Ephedraceae), *Achillea aleppica* DC. (Asteraceae), *Silene conoidea* L. (Caryophyllaceae), *Centaurea virgate* Lam. (Asteraceae), *Askellia corniculata* (Regel and Schmalh.) W.A. Weber (Asteraceae), and a few Species of *Astragalus* L. (Fabaceae). Seven samples of *Ephedra* and eight samples of *Achillea* were collected along with soil samples considering their widespread distribution in the vicinity of Dashkasan mine and consumption as medicinal plants. Moreover, these plant species are used as livestock's fodder in the study area. The samples were rinsed with deionized water to remove any attached dust and pollen particles. Damaged parts were removed and the plants were dried for 14 days at room temperature. 0.5 g of each dry sample was mixed with concentrated nitric acid and hydrogen peroxide and sealed in a digestion vessel. After digestion, distilled water was added to dilute the acid solution and samples were kept in test tubes.

Plant leaves were analyzed for their major and trace element concentrations in Acme Analytical Laboratories, Canada using inductively coupled plasma mass spectrometry (ICP-MS).

Biological concentration factor (BCF) is widely used for comparing different plants tendency for metal uptake according to the following equation:

$$BCF = \frac{C_p}{C_s}$$

where  $C_p$  is the concentration of elements in the above ground part of the plant and  $C_s$  is the total concentration in soil (Rotkittikhun et al. 2006).



The translocation factor (TF) for metals within a given plant was calculated by dividing metal concentration in the stem and leaves to that in the root (Rizzi et al. 2004).

## Results and discussion

### Environmental geochemistry of epithermal gold deposits

Epithermal gold deposits also known as shallow high- and low sulfidation Cu–Au–Ag deposits encompass a large spectrum of mineral deposits that include high sulfidation-type Au–Ag–Cu deposits, low sulfidation-type Au–Ag deposits and subtypes such as hot spring Au deposits bound to subaerial siliceous sinter (Dill 2010). These terms refer specifically to the oxidation state of sulfur in the ore-forming fluid, the chemistry and pH of which is related to the nature of alteration associated with each type (Robb 2005). Many studies showed that epithermal deposits typically form at temperatures between 160 and 270 °C and pressures equivalent to depths of 50–1000 m (Cooke and Simmons 2000; Hedenquist et al. 2000).

During the reaction between ore-bearing hydrothermal fluids and wall-rocks, some elements are concentrated in specific locations to form hydrothermal ore deposits (Zhu et al. 2011). Table 3 summarizes the main characteristics of low- and high-sulfidation epithermal deposits.

Geoenvironmental signatures associated with different parts of epithermal vein deposits are highly variable on all scales due to well-developed spatial zonation within vein and alteration mineral assemblages (Plumlee et al. 1995a).

Based on the sulfidation state of hydrothermal gold deposits, their potential environmental effects are different. In high sulfide type epithermal gold deposits, central advanced argillic zone has iron-, copper-, and arsenic-rich

sulfide and sulfosalt minerals with high acid generating capacity (pH 1.5–3) which contains high abundance of toxic metals (Plumlee et al. 1995b). These deposits are hosted by felsic volcanic rocks, generally intrusions or lava domes that have low acid buffering capacity (Berger 1986).

Predominant downstream signatures include elevated abundances of acid, iron, aluminum, manganese, and copper. Iron and aluminum form hydrous oxide precipitates as a result of dilution by downstream tributaries, and help sorb some of the dissolved metals (Smith et al. 1995).

The low sulfide type Au deposits are associated with bimodal (basalt–rhyolite) volcanic suites, silicic to intermediate and alkali volcanic host rocks (Henley 1991). In many districts, host volcanic rocks are altered to propylitic assemblages, including chlorite, epidote, calcite, and albite. Therefore, waters interacting with the ore deposit are generally non-acidic, likely due to the low sulfidation system, as well as the limited extension of the ore veins and the weathering of silicate rocks (Biddau and Cidu 2005). The nonacid environment does not favor the mobility of elements associated with the mineralization, such as Cd, Co, Ni, Pb, Zn, and As (Plumlee et al. 1995a). In addition, Biddau and Cidu (2005) reported that aqueous transport of these elements seems to be limited by the precipitation of ferrihydrite, which is able to reduce or remove these elements, particularly As, from solution.

### Elements in soil

Hydrometry and sieve analysis showed that on the basis of Folk's (1980) classification soil texture in the study area is mostly poorly sorted muddy sand. Since the exposed lithologies surroundings the Dashkasan ore deposit is predominantly felsic to intermediate volcanic rocks (dacitic and rhyodacitic domes) and, to a lesser extent, metamorphic and sedimentary, it is not surprising that the soil

**Table 3** Characteristics of high and low sulfide epithermal gold deposits (modified after Hayba et al. 1985; Henley 1991; Robb 2005)

	High-sulfidation	Low-sulfidation
Fluid solution redox	Oxidized sulfur species ( $\text{SO}_2$ , $\text{SO}_4^{2-}$ , $\text{HSO}_4^-$ ) in ore fluid/vapor	Reduced sulfur species ( $\text{HS}^-$ , $\text{H}_2\text{S}$ ) in ore fluid/vapor
Host rocks	Rhyodacite typical	Silicic to intermediate and alkali volcanics
Size	Relatively small	Variable, some very large
Also referred to as	Gold–alunite, acid–sulfate, alunite–kaolinite	Adularia–sericite, hot spring-related
Fluids	Acidic pH, probably saline initially, dominantly magmatic	Near-neutral pH, low salinity, gas-rich ( $\text{CO}_2$ , $\text{H}_2\text{S}$ ), dominantly meteoric
Alteration	Advanced argillic (zonation: quartz–alunite–kaolinite–illite–montmorillonite–chlorite)	Adularia–sericite–probilitic (zonation: quartz/chalcedony–calcite–adularia–sericite–chlorite)
Metal associations	Au–Cu (lesser Ag, Bi, Te)	Au–Ag (lesser As, Sb, Se, Hg)

mineralogy and the elemental composition are closely related to the acidic and intermediate volcanic rocks in the region. Soil pH ranged from 7.15 to 7.75; therefore, Dashkasan soil was classified as neutral to sub-alkaline.

The measured concentrations of 18 elements together with mean, median and standard deviation (SD) in soil samples and from undisturbed control site are summarized in Table 4 along with concentrations in world natural soils (WNS) and the Earth's crust for comparison. It can be seen that only Ni and Cr mean contents are lower than world natural soils (Table 4).

When compared with natural soils, Dashkasan soil is characterized by elevated concentrations of Ag, As, Au, Sb, Hg, Bi, Ni and Pb, especially in the vicinity of the waste dumps. The most pollutant metal is Ag, reaching 10,220 mg kg<sup>-1</sup> in soils near the waste dumps. Ag-rich soils (6 and 9) also show high Pb, Hg, Sb and Au content.

As concentration in Dashkasan soil samples averaged 1696.68 mg kg<sup>-1</sup> which is much higher than natural soil values (1–10 mg kg<sup>-1</sup>) (Koljonen 1992) or soils formed on mineralized bedrocks (726 mg kg<sup>-1</sup>) (Abrahams and Thornton 1987), or soils close to non-ferric metal mining (90–100 mg kg<sup>-1</sup>) (Colbourn et al. 1975). Considering the absence of industrial plants in the study area, the origin of arsenic in the soils is assumed to be mainly geogenic related to erosion of the As-rich epithermal ores and related alteration zones along with mining activity. The occurrence of arsenical pyrite in veins and wall rocks (Niroomand et al. 2013) is probably the main source of arsenic in Dashkasan soil.

Mercury concentration in Dashkasan soil ranges between 0.15 and 50 mg kg<sup>-1</sup>. All samples exhibit higher values than background (1.13 mg kg<sup>-1</sup>) and natural (1.1 mg kg<sup>-1</sup>) soils (Kabata-Pendias 2011).

Mercury commonly occurs as cinnabar (HgS) in veins, or substitutes for other elements in pyrite, marcasite, and stibnite. Craw et al. (2000) showed that minor mercury occurs in solid solution in marcasite in hydrothermal systems. Marcasite readily decomposes during oxidation and mercury, which is temporarily adsorbed on or absorbed in ironhydroxides, is released to the environment (Craw 2001).

Sb concentration in Dashkasan soil ranges between 1.10 and 2000 mg kg<sup>-1</sup> averaging 362.95 mg kg<sup>-1</sup>. Sb concentration in all samples except sample No 15, is above the natural content (0.67 mg kg<sup>-1</sup>) (Kabata and Pendias 2001) and local background (0.71 mg kg<sup>-1</sup>) soils. It is roughly comparable to the previously reported Sb concentration in mining areas of Scotland and China (He and Yang 1999; Gal et al. 2007). Chalcophile Sb is commonly associated with sulfidic ore deposits. In Dashkasan area, antimony (as stibnite) is a major component of mineralized veins in the hydrothermal system (Rastad et al. 2000; Richards et al. 2006; Niroomand et al. 2013). Hence, mining activity and

weathering of Sb bearing minerals are assumed to be the main sources of antimony pollution in Dashkasan soil.

Soil Au content is very high averaging 3.58 mg kg<sup>-1</sup>, which reflects a significant pollution impact compared to the average global Au concentration in soils (0.001–0.002 mg kg<sup>-1</sup>) (Kabata and Pendias 2001), and the local background value of 0.003 mg kg<sup>-1</sup>. Elevated Au contents (up to 5.0 mg/kg) have also been reported in soils at Au mining areas of US and Southern Australia (Lakin 1974; Lottemoser 1995). Apparently anomalous Au contents at Dashkasan are the result of epithermal mineralization. Au is an incompatible element, and tends to concentrate in residual melts. It is already mentioned that in Dashkasan ore deposit arsenical pyrite and arsenopyrite are gold host minerals. Gold replaces Fe<sup>2+</sup> in arsenopyrite (Tarnocai et al. 1997; Cabri et al. 2000).

Pb concentration in soil samples varies between 47.91 and 3150 mg kg<sup>-1</sup> averaging 479.06 mg kg<sup>-1</sup> exceeding the local background (21.37 mg kg<sup>-1</sup>), world soils (27 mg kg<sup>-1</sup>), and crustal abundance (15 mg kg<sup>-1</sup>) (Kabata-Pendias 2011). According to Richards et al. (2006), Pb concentration in Dashkasan ore deposit ranges between 23 to 169 mg kg<sup>-1</sup> being above the crustal abundance (Levinson 1980). Lead occurs as galena and is commonly associated with gold mineralization; thus, during ore crushing lead is released into the environment (Ogola et al. 2002). In mining areas, Pb may be dispersed due to erosion and chemical weathering of tailings depending on chemical characteristics and the minerals present in the tailings (Ferreira da Silva et al. 2004). Moreover, Pb has an ability to replace K, Ba, Sr, and even Ca and Na both in mineral lattices and in sorption sites (Kabata-Pendias 2011; Nriagu 1978). Consequently, weathering of Pb host minerals, for example galena (PbS), cerussite (PbCO<sub>3</sub>) and bolangerite (Pb<sub>5</sub>Sb<sub>4</sub>S<sub>11</sub>) in addition to mining activity, can disperse Pb into the soil environment and cause Pb pollution.

As already mentioned, some other analyzed trace elements also exhibit mean concentrations slightly higher than world natural soils (e.g., Ni, Mo, Cu, Cd, Zn, U and Mn). The exceptions are Fe, Al and Cr which are depleted relative to the world mean concentrations. It is noteworthy that once erosion starts, the unroofing of a mineral deposit may lead to the massive and sustained leaching of metals and, therefore, to long-lived 'natural contamination' of the surrounding environment. The longer the process, the greater is the effect (Oyarzun et al. 2004).

### Inter-elemental relationships

Inter-elemental relations can provide information on heavy metal sources and pathways (Imperato et al. 2003; Lu and Bai 2010). To describe the degree of association between different elemental variables, spearman correlations matrix (Table 5) and cluster analysis (CA) (Fig. 2) were carried out.

**Table 4** Element concentrations ( $\text{mg kg}^{-1}$ ) and pollution load index (PLI) in Dashkasan top soil samples

	Fe (%)	Al (%)	S (%)	As	Bi	Cd	Cr	Cu	Mo	Mn	Ni	Pb	U	Sb	Zn	Ag (ppb)	Au (ppb)	Hg (ppb)	PLI
DL <sup>a</sup>	0.01	0.01	0.02	0.1	0.02	0.01	0.5	0.01	0.01	1	0.1	0.01	0.1	0.02	0.1	2	0.2	5	–
1	3.5	1.8	0.13	338	1.49	0.74	41	21.83	1.24	580	52.9	115.5	2.3	24.11	96.9	458	387.5	518	4.38
2	2.82	1.56	0.07	205.3	1.27	0.76	43.5	25.97	0.95	665	57.6	101.5	1.4	9.2	98.7	401	131.4	154	3.21
3	4.19	1.19	0.39	1908	3.31	10.92	29.4	58.97	<0.01	184	48.7	382.5	13.9	1899	88.1	3238	17,332	50,000	12.99
4	2.86	1.14	0.27	975.2	2.91	0.57	35.2	47.49	5.9	382	45.2	3150	3	47.4	58	8099	232.4	3631	8.69
5	3.6	1.72	0.03	411.8	1.55	0.73	42.7	62.5	1.32	1225	57.6	1345	1.7	11.52	144.3	2321	48	729	5.07
6	5.72	1.03	3.67	10,000	0.53	0.41	26.2	13.31	14.29	79	51.8	185.7	4.5	1323	70.2	3200	6629	50,000	13.58
7	3.03	1.66	0.15	546.7	3.53	0.71	47.9	24.44	1.51	397	48.4	249.9	10.6	28.22	73.8	1452	599	4550	6.71
8	3.19	1.58	0.25	228.9	0.40	0.57	47.8	25.38	1.31	438	48.2	110	2.1	61.89	76.9	371	313	11,347	4.87
9	3.29	0.7	3.19	10,000	1.55	0.64	4.1	0.0075	12.36	0.75	28.2	831.4	10.3	2000	54.5	10,220	27,867	50,000	8.36
10	2.32	1.44	0.07	143.4	0.27	0.35	42.8	23.16	1.02	449	52.8	83.53	2.2	13.51	61.4	132	25	1591	2.59
11	2.78	1.41	0.05	63	0.39	0.47	37.2	20.22	0.92	664	44.5	123.5	2.6	3.67	98.4	160	4.7	540	2.11
12	3.45	2.18	0.02	55.3	0.35	0.31	58.7	25.94	0.83	879	72.2	47.91	0.9	3.89	96.1	65	15.2	705	1.96
13	2.78	1.69	0.14	126.8	1.82	0.23	39.3	18.16	1.18	425	48.9	114.6	1.4	9.65	57.2	577	44.1	264	2.85
14	3.35	1.73	0.07	355.6	0.69	0.95	40.3	26.2	1.32	974	58.9	259.2	1.7	8.05	202.6	514	28	852	3.86
15	2.62	1.53	0.10	92.2	1.53	0.45	50	22	0.9	343	42.3	85.64	2.3	1.1	60.3	171	9.5	381	2.15
Mean	3.30	1.49	0.57	1696.68	1.43	1.25	39.07	27.71	3.00	512.31	50.55	479.06	4.06	362.95	89.16	2092	3.58	11.68	–
Median	3.19	1.56	0.13	338	1.49	0.57	41.00	24.44	1.24	438	48.90	123.50	2.30	13.51	76.90	514	0.13	0.85	–
S.D	0.81	0.36	1.16	3404.48	1.08	2.68	12.57	16.50	4.40	331.63	9.63	818.16	4.06	726.47	39.40	3091	8.15	20.04	–
Min	2.32	0.7	0.02	55.30	0.27	0.23	4.10	0.01	0.01	0.75	28.20	47.91	0.90	1.10	54.50	65	0.004	0.15	–
Max	5.72	2.18	3.67	10,000	3.53	10.92	58.70	62.50	14.29	1225	72.20	3150	13.90	2000	202.60	10,220	27.87	50.00	–
L.B <sup>b</sup>	1.9	1.61	0.02	23.6	0.2	0.25	35.8	17.02	0.4	501	45.7	21.37	0.9	0.71	47.2	63	0.003	0.13	–
Clark <sup>c</sup>	5	8.2	260	1.8	0.2	0.1	100	55	1.5	950	20	15	0.9–1.7	0.2	70	60	4.1	70	–
W.N.S <sup>d</sup>	3.50	6.65	433	6.83	0.42	0.41	54	20	1.80	437	29	27	2.18	0.67	64	130	3	1100	–

<sup>a</sup> Detection limit

<sup>b</sup> Local background

<sup>c</sup> Average crustal abundance of elements from Wedepohl (1986), Bowen (1979) and Kabata-Pendias (2011)

<sup>d</sup> Average content in world natural soils, from Bowen (1979) and Kabata-Pendias (2011)

**Table 5** Spearman correlation coefficients (*r*) for soil elements

	Zn	U	Sb	Pb	Ni	Mo	Mn	Hg	Fe	Cu	Cr	Cd	As	Au	Al	Ag	S	Bi
Zn	1.00																	
U	-0.36	1.00																
Sb	-0.39	<b>0.62*</b>	1.00															
Pb	0.00	<b>0.53*</b>	<b>0.51*</b>	1.00														
Ni	<b>0.64**</b>	-0.64**	-0.29	-0.24	1.00													
Mo	-0.25	0.30	<b>0.53*</b>	<b>0.58*</b>	-0.15	1.00												
Mn	<b>0.80**</b>	-0.74**	-0.62*	-0.23	<b>0.72**</b>	-0.27	1.00											
Hg	-0.28	<b>0.68**</b>	<b>0.82**</b>	0.50	-0.30	0.48	-0.55*	1.00										
Fe	0.35	0.20	0.48	0.44	0.37	0.27	-0.02	0.48	1.00									
Cu	<b>0.52*</b>	-0.20	-0.08	0.26	0.42	-0.22	0.46	0.01	0.23	1.00								
Cr	0.25	-0.51	-0.55*	-0.66**	0.31	-0.42	0.47	-0.46	-0.32	0.26	1.00							
Cd	<b>0.55*</b>	0.26	0.25	<b>0.51*</b>	0.15	0.06	0.15	0.15	0.42	<b>0.52*</b>	-0.16	1.00						
As	-0.19	<b>0.66**</b>	<b>0.84**</b>	<b>0.78**</b>	-0.19	<b>0.69**</b>	-0.52*	<b>0.75**</b>	<b>0.58*</b>	0.07	-0.63*	0.48	1.00					
Au	-0.25	0.60*	<b>0.92**</b>	<b>0.52*</b>	-0.19	<b>0.52*</b>	-0.58*	<b>0.67**</b>	<b>0.58*</b>	-0.07	-0.49	0.44	<b>0.87**</b>	1.00				
Al	<b>0.54*</b>	-0.68**	-0.51*	-0.34	<b>0.68**</b>	-0.26	<b>0.75**</b>	-0.54*	0.11	0.29	<b>0.64**</b>	0.06	-0.50	-0.38	1.00			
Ag	-0.30	<b>0.57*</b>	<b>0.72**</b>	<b>0.87**</b>	-0.28	<b>0.63*</b>	-0.53*	<b>0.55*</b>	0.47	0.06	-0.71**	0.40	<b>0.90**</b>	<b>0.77**</b>	-0.47	1.00		
S	-0.61*	<b>0.70**</b>	<b>0.83**</b>	0.42	-0.54*	0.50	-0.88**	<b>0.67**</b>	0.26	-0.32	-0.58*	0.09	<b>0.74**</b>	<b>0.81**</b>	-0.64**	<b>0.71**</b>	1.00	
Bi	-0.29	0.46	0.38	<b>0.63*</b>	-0.33	0.24	-0.42	0.16	0.15	0.20	-0.26	0.40	0.53*	<b>0.52*</b>	-0.15	<b>0.75**</b>	0.47	1.00

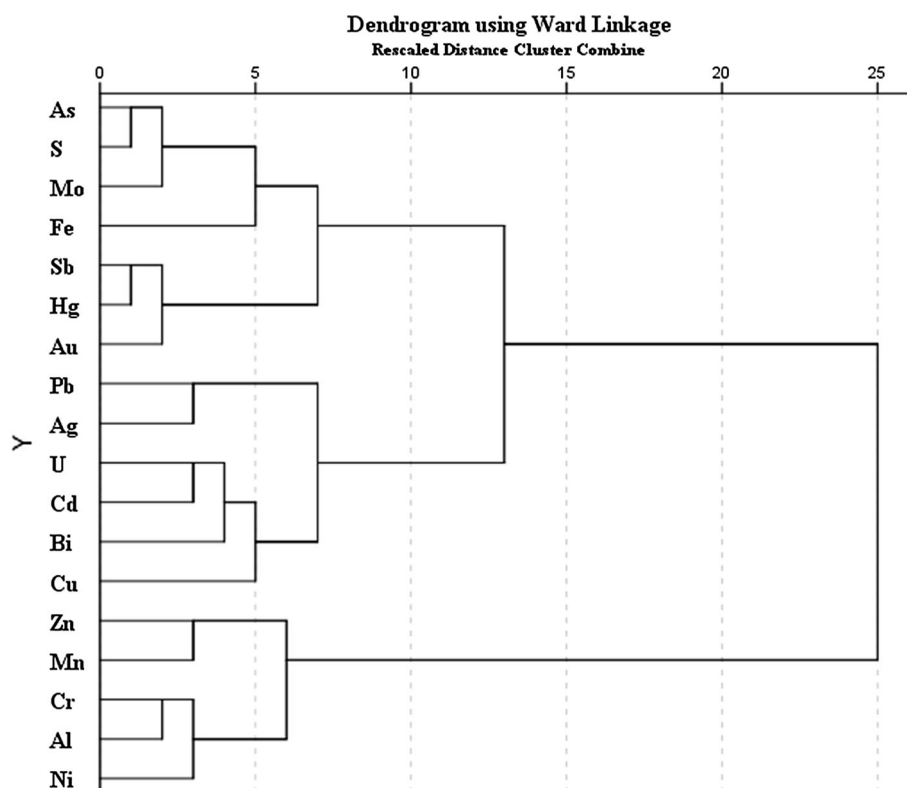
Significant correlation values are shown in bold

\*\* Correlation is significant at the 0.01 level (2-tailed)

\* Correlation is significant at the 0.05 level (2-tailed)



**Fig. 2** Hierarchical dendrogram for the elements obtained using Ward's clustering method



A significant characteristic of the soil in Dashkasan mine area is the highly significant correlation (0.55–0.92) between Au, Sb, As, Hg and Ag. Similarly, Bi, Pb, U and Cd in soil are markedly positively correlated. Tumuklu et al. (2007) suggested that heavy metals with high and medium positive correlation probably come from the same source. The observed correlations suggest a close link with polymetallic mineralization and common geochemical characteristics. Richards et al. (2006) revealed that in Dashkasan ore deposit, epithermal veins are characterized by an increasing abundance of chalcophile element-bearing minerals throughout the paragenesis.

The significant positive correlation with sulfur confirmed that soil elements at Dashkasan are closely related to sulfide mineralization. Sulfidic ligands are essential in metal-transporting fluids, enhancing the solubility of gold and possibly copper by the formation of stable metal–sulfide complexes (Mountain and Seward 2003; Stefánsson and Seward 2004) in subcritical aqueous solutions, as required for the formation of epithermal gold deposits (Ronacher et al. 2004). Obviously, mining operations in Dashkasan mine have enhanced metal pollution in the soil environment. Cr and Ni displayed negative or weak correlation with most of the analyzed elements due to different behavior during magmatic differentiation.

The positive correlation between Fe and most heavy metals reflects association of iron with these elements in sulfide minerals (e.g., pyrite, chalcopyrite). Furthermore,

Fe in iron minerals (e.g., siderite, hematite and magnetite) occurs in different polymetallic veins in the host rock. It is known that Fe oxides/hydroxides are effective scavengers of heavy metals in oxic environments (Arakel and Hongjun 1992; Aubert et al. 2004) and highly affect trace element mobility in soils.

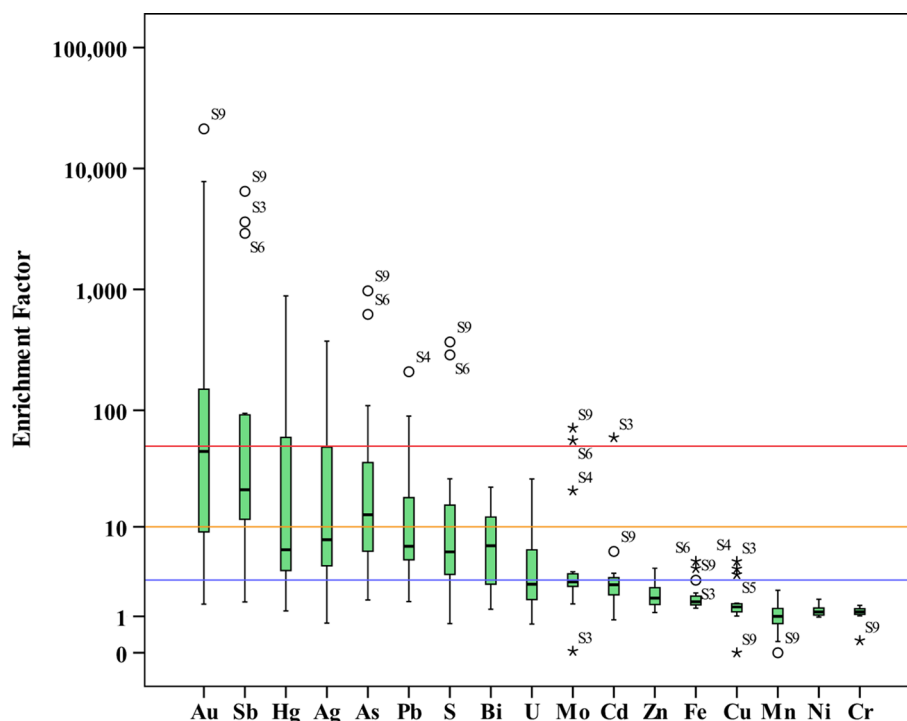
The weak or negative association of trace elements with manganese and aluminum suggests that their abundance and distribution are not significantly controlled by the soil's clay minerals and Mn-hydroxide (Zhuang et al. 2009). The cluster analysis for the soil heavy metal contents in the study area is illustrated in Fig. 2.

All values were standardized using z scores before CA; then, the Euclidean distances among the values were calculated. Finally, hierarchical clustering was performed using Ward's method (Guillén et al. 2012; Zheng et al. 2013). In general, the results of CA are in good agreement with those of correlation matrix. Two distinct clusters are observed for the metals in soils. Cluster I contains As, S, Mo, Fe, Sb, Hg, Au, Pb, Ag, U, Cd, Bi and Cu and represents the contribution of sulfide minerals in releasing chalcophile elements through weathering anthropogenic activity.

### Heavy metal pollution

Soil enrichment factors are represented in Fig. 3. EF values displayed the following decreasing trend: Au >> Sb > Hg

**Fig. 3** Box plots of the EF of some selected elements in soil samples



> Ag > As > Pb > S > Bi > U  $\gg$  Mo > Cd > Zn  $\approx$  U, Fe, Cu, Mn, Cr, Ni. The trend is consistent with those obtained by CA and correlation matrix. It is obvious that EF variations are greater in the first nine elements (Fig. 3).

EF value of 1.5 generally indicates lithogenic sources. To discriminate anthropogenic and natural sources for a given element, EF estimates should be >10 (Zhang et al. 2007b). However, Hernandez et al. (2003) mentioned that while EF values between 0.5 and 2 should be considered in the range of natural variability, ratios >2 may indicate enrichment corresponding to anthropogenic input. Dashkasan results indicate that soil samples are moderate to extremely highly enriched in Au, As, Hg, Ag, As, Pb, S, Bi, U and Mo. The enrichment is mostly due to both ore mineralization and past and ongoing anthropogenic activities (mining operation) in the study area. High EF values occur close to the tailing piles (S9 and S6) and polymetallic veins in the vicinity of the so-called Sari-Dagh domes (S3 and S4). Rastad et al. (2000) indicated that Sari-Dagh dome contains numerous gold-bearing veins, where Mo, Cd, Zn, Cu and Fe EF vary between 0 and 4.61 indicating lack of enrichment to moderate enrichment resulting from their mixed sources. On the contrary, Mn, Ni and Cr showed no enrichment indicative of their natural source.

The results of calculated contamination factors (CF) (Fig. 4) are consistent with EF results. CF displayed the following decreasing trend:

Au  $\gg$  Sb > Hg > Ag > As > Pb > S > Bi > U > Mo > Cd > Zn > Fe > Cu > Mn > Cr > Ni.

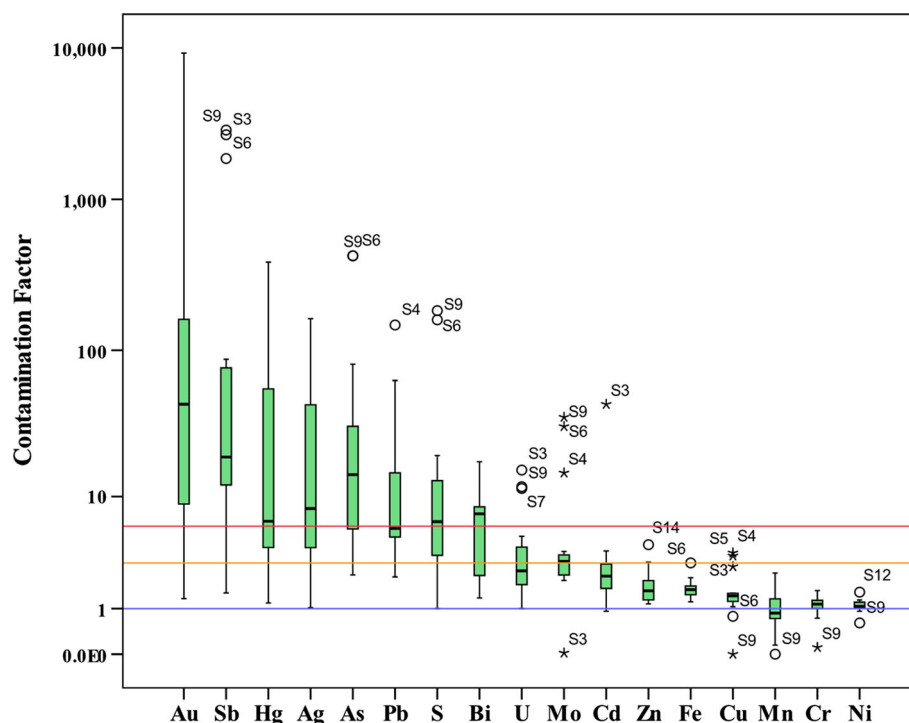
According to Hakanson (1980), Au, Sb, Hg, Ag, As, Pb, S and Bi display moderate to extremely high contamination, while U, Mo, Cd, Zn, Fe and Cu show moderate to considerable contamination and Mn, Cr and Ni reveal minimal to moderate contamination. Generally speaking, the results obtained from enrichment and contamination factor calculations confirm those obtained from cluster analysis and correlation matrix. Overall, it can be concluded that elements with high EF and CF are affected by mineralization and mining activity.

Pollution severity was determined using pollution load index (PLI). The results are presented in the last column of Table 4. The results show that PLI in all stations is higher than 1, reflecting mineralization, high concentration in parent rocks, and dispersion of metals due to mining. The high PLI of samples 6 and 9 is probably the result of open waste dumping.

### Elements in plants

Heavy element concentrations in the leaves and roots of two indigenous sampled plants are summarized in Table 6. Despite high total concentrations of trace metals in soils (Table 4), plants did not show high metal content in their tissues (Table 6) and the two analyzed plant genuses displayed relatively similar elemental contents in the leaves. However, higher concentrations of Al, As, Au, Fe, Hg, Pb, Sb, U, Ag and Zn were noted in *Ephedra* species, while some other elements showed higher concentration in

**Fig. 4** CF box plots of selected elements in Dashkasan soil samples



*Achillea* samples. Generally, the mean concentrations of all elements except Fe are below the toxic range for plants (Table 6).

While the average As content in *Ephedra* and *Achillea* (3.17 and 0.53 mg kg<sup>-1</sup>, respectively) is in the range of average As content in plant tissues (<0.01–4 mg kg<sup>-1</sup>) (NRC 1977), maximum concentration of As in *Ephedra* (7.70 mg kg<sup>-1</sup>) and *Achillea* (1.1 mg kg<sup>-1</sup>) is higher than As tolerance range (2 mg kg<sup>-1</sup>) and toxic range for plants (5–20 mg kg<sup>-1</sup>) (Kabata-Pendias 2011).

Average Au content in *Ephedra* is  $3.4 \mu\text{g kg}^{-1}$ , which is higher than  $0.3 \mu\text{g kg}^{-1}$  observed in *Achillea*. According to Greger (1999), average Au content in plants is  $1 \mu\text{g kg}^{-1}$ . Au in plants and shrubs in different parts of the world are extensively investigated in biogeochemical surveys for Au mineralization (Vernadsky 1997). Maximum Au concentration in *Ephedra* and *Achillea* is  $15.4$  and  $0.6 \mu\text{g kg}^{-1}$ , respectively, which resembles the range of gold concentration in plants of gold mining areas ( $3\text{--}19 \mu\text{g kg}^{-1}$ ) reported by Davies (1997).

The mean Cd content was 0.50 and 1.49 mg kg<sup>-1</sup> in *Ephedra* and *Achillea*, respectively, and is higher than the threshold value of 0.32 mg kg<sup>-1</sup> in grasses and 0.35 mg kg<sup>-1</sup> in clover, but is lower than toxic range for plants (6–10 mg kg<sup>-1</sup>) reported by Kabata-Pendias (2011). Thus, high concentration of cadmium in both species may inhibit plant growth and pose a threat to livestock and local population health. Mean lead concentration in *Ephedra* samples (0.9 mg kg<sup>-1</sup>) is higher than *Achillea*

(0.38 mg kg<sup>-1</sup>). Maximum concentration of Pb in *Ephedra* (2.31 mg kg<sup>-1</sup>) and *Achillea* (0.9 mg kg<sup>-1</sup>) is lower than critical toxicity level for plants (30–300 mg kg<sup>-1</sup>) (Pais and Jones 1997). Average Sb content of *Ephedra* and *Achillea* is 0.9 and 0.3 mg kg<sup>-1</sup>, respectively, which is much higher than the range of Sb in crop plants growing in soils of historical mining areas (Kabata-Pendias and Mukherjee 2007) and mean Sb content in terrestrial plants (Bowen 1979). Maximum concentration of antimony (3.84 mg kg<sup>-1</sup>) was observed in *Ephedra* samples in the vicinity of mineralized veins of eastern Sari-Dagh dome. The concentration of most other elements is nearly in the normal range and does not reach toxic level in the two analyzed plant species.

Table 6 illustrates the biological concentration factor (BCF) calculated for each element. Higher BCF reflects relatively poor retention in soils or greater efficiency of plants to absorb metals, while low coefficients indicate strong sorption of metals to the soil colloids (Cui et al. 2004; Kachenko and Singh 2006). Singh et al. (2011) demonstrated that  $BCF < 1$  denotes that the plant only absorbs but does not accumulate heavy metals, while  $BCF > 1$  indicates that plant accumulates metals. The decreasing trend of mean BCF for elements in *Ephedra* is  $Cd > Zn > Mo, Mn, Cu > Cr, Hg, Ni, Al > Fe, U, Pb, Au, Sb$  and  $As$  and in *Achillea* is  $Mo > Cd > Zn, Cu, Mn > Cr, Ni, Al, Sb > Fe, Hg, Au, Pb, U$  and  $As$ . The order in both species confirms previous studies indicating that  $Cd$  is the most, and  $As$  the least, readily accumulated

**Table 6** Total element mean concentrations ( $\text{mg kg}^{-1}$ ) and biological concentration factor (BCF) in studied plant species

DL <sup>a</sup>	<i>Ephedra</i>				<i>Achillea</i>				Range in plant tissues (mg/kg dw) <sup>b</sup>	Sufficient or normal <sup>i</sup>	Range toxic for plants <sup>i</sup>	Threshold for hyperaccumulators (mg/kg dry weight) <sup>j</sup>	Mining, or mineralized Area (mg/kg)
	Leaf and stem				Leaf and stem								
	Min	Max	Mean	BCF	Min	Max	Mean	BCF					
Al	10	200	400	257.14	0.018	100	300	212.50	0.017	–	–	–	–
As	0.1	0.10	7.70	3.17	0.003	0.10	1.10	0.53	0.001	<0.1–4 <sup>c</sup>	–	>1000	140–6640
Au	0.2	0.2	15.4	3.4	0.007	0.2	0.6	0.3	0.004	0.001 <sup>d</sup>	–	0.1–100 <sup>i</sup>	0.003–0.019 <sup>n</sup>
Cd	0.01	0.08	1.42	0.58	10.747	0.20	4.97	1.76	1.120	0.03–0.5	0.05–0.2	>100	0.1–22
Cr	0.1	1.60	2.20	1.96	0.054	1.10	2.70	2.14	0.064	0.2–1	0.1–0.5	>1000	–
Cu	0.01	1.63	3.04	2.34	0.105	5.36	10.49	7.98	0.326	2–20	5–30	>1000	–
Fe	1	230	440	300	0.009	120	330	250.00	0.008	43–400 <sup>e</sup>	20–200 <sup>j</sup>	–	–
Hg	1 ppb	0.022	0.028	0.025	0.034	0.003	0.009	0.006	0.008	0.005–0.2	–	>1000	0.04–37.6
Mn	1	24	31	27.86	0.118	26.00	38	31.50	0.139	1–700	20–300 <sup>j</sup>	>10,000	–
Mo	0.01	0.08	0.39	0.21	0.132	0.04	0.42	0.22	3.428	0.07–1.75	0.2–5	–	–
Ni	0.1	1.30	2.20	1.66	0.033	1.20	2.60	1.75	0.034	0.4–4	0.1–5	>1000	–
Pb	0.01	0.29	2.31	0.90	0.008	0.05	0.90	0.38	0.002	0.1–5	5–10	>1000	63–570
Sb	0.02	0.04	3.84	0.90	0.006	0.07	0.81	0.30	0.015	0.06 <sup>g</sup>	7–50	>1000 <sup>m</sup>	<20–1130 <sup>e</sup>
U	0.01	0.01	0.08	0.03	0.009	0.01	0.01	0.01	0.002	0.005–0.06 <sup>g</sup>	–	–	2.2
Zn	0.1	14.90	53.80	31.47	0.410	18.80	38.90	29.38	0.402	15–150	27–150	>10,000	39–710
S	10	1100	1700	1500	–	1200	2000	1566	–	1000–5000 <sup>h</sup>	–	–	–
Bi	0.02	BD	0.05	–	–	BD	BD	–	–	<0.02 <sup>g</sup>	–	–	–
Ag	0.002	0.004	0.022	0.011	–	BD	BD	–	–	0.03–2.9	0.5	–	–

<sup>a</sup> Detection limit<sup>b</sup> From Maestri et al. (2010)<sup>c</sup> From NRC (1977)<sup>d</sup> Au content in reference plant from Greger (1999)<sup>e</sup> From Kabata-Pendias and Mukherjee (2007)<sup>g</sup> Content in terrestrial plants from Bowen (1979)<sup>h</sup> Typical range in food crops compiled by Alloway (2013)<sup>i</sup> From Kabata-Pendias (2011)<sup>j</sup> From Pais and Jones (1997)<sup>k</sup> Ecotoxicity threshold for terrestrial plants from Sheppard et al. (2005)<sup>l</sup> From Fasani (2012)<sup>m</sup> From Chaney et al. (1997)<sup>n</sup> From Davies (1997)

trace elements in vegetation (Alvarenga et al. 2004; Batista et al. 2007; Jung and Thornton 1996; Madejón and Lepp 2007). The difference in BCF probably reflects different physiological characteristics and uptake behavior.

BCF revealed high Cd accumulation in both species (10.747 and 1.120 in *Ephedra* and *Achillea*, respectively) indicative of weak retention of  $\text{Cd}^{2+}$  by the soil (Lokeshwari and Chandrappa 2006). Previous studies have already indicated that an appreciable fraction of soil Cd is taken up passively and metabolically by plant roots (Smeyers-Verbeke et al. 1978). Moore et al. (2014) also indicated that Cd is more bioavailable to *Artemisia*, *Astragalus* and *Acanthophyllum* plant species in Miduk porphyry copper mining area, Iran.

In aerobic conditions, Mo occurs mainly as molybdate oxyanion and Plants Mo uptake occurs as molybdate ions (Kabata-Pendias 2011). Despite high enrichment factor values of soil samples (11.89 in average), Mo accumulation in plants is low. The results obtained from BCFs show that Mo accumulation in plants is higher than most elements (Table 6); its concentration in plant samples fall within the optimum range for plant metabolism (0.1–0.5) as reported by Kabata-Pendias and Mukherjee (2007). The higher BCF probably demonstrates the dominance of the plant's genetics influence on element uptake and active uptake of Mo by plants (Kabata-Pendias 2011).

Low lead BCFs in *Ephedra* and *Achillea* (0.008 and 0.002, respectively) could be due to low solubility at pH values above 4 (Evans et al. 1995), which also agrees with Kabata-Pendias and Mukherjee (2007) who also showed that Pb absorption by root is passive and its uptake from soils is rather low. Kabata-Pendias and Pendias (1992) reported that lead is usually not highly available to plants, because it occurs in water-insoluble chemical species. Del Rio et al. (2002) demonstrated that lead concentration in the shoots of plants growing on soils that contained up to  $1000 \text{ mg kg}^{-1}$  lead ranged between 5 and  $50 \text{ mg kg}^{-1}$ .

Arsenic displayed the lowest BCF in both species (0.003 and 0.001 in *Ephedra* and *Achillea*, respectively). Very similar patterns were obtained by Madejón and Lepp (2007) which also found low soil to root transfer factor in different plant species growing in soils with high As content. The reason is probably low availability of As in soil (Kloke et al. 1984). Based on Table 6, Cd, Mo, Zn and to some extent Cu and Mn are more bioavailable to the two investigated plant species.

Considering the high affinity of metals for sulfur in soil samples, the relatively low total concentration of toxic elements in plants, and the low calculated BCF values, it is not surprising that most metals displayed low bioavailability and hence are not toxic to plant species.

## Conclusion

Soils in the vicinity of Dashkasan mining area in Iran revealed long-term geogenic contamination due to natural mineralization. Apparently, discontinuous anthropogenic mining activity in the area has enhanced weathering processes of ore minerals and scattered tailing piles, which in turn resulted in vast dispersion of ore-forming elements in the study area. Calculated enrichment and contamination factors indicate that Dashkasan soil is significantly contaminated with Ag, Au, As, Hg, Sb, Pb, S and Bi. Calculation of pollution load index revealed high levels of pollution in all sampling stations.

Analysis of two indigenous medicinal plant species indicated that total concentrations of Al, As, Au, Fe, Hg, Pb, U, Sb and Zn in *Ephedra* are generally higher than those in *Achillea*, while some other analysed elements displayed higher concentration in *Achillea* samples. No significant accumulation was observed for Al, Cu, Hg, Mn, Mo, Ni and Zn in the two investigated plant species. Cd, Mo, Zn and to some extent Cu and Mn seem to be more bioavailable to the examined plant species in Dashkasan mining area.

Calculated BCFs indicated that *Ephedra* species is a good accumulator of cadmium, while *Achillea* is an efficient accumulator of both Cadmium and Molybdenum.

Statistical analyses indicated high affinity of metal for sulfur in the soil. Moreover, low BCF and relatively low total metals content in the analyzed plant species confirmed that most chalcophile metals exhibit low bioavailability with no toxicity for plant species.

Rural population living in the vicinity of Dashkasan area consumes *Achillea* for treatment of cold and urinary tract disorders and *Ephedra* for asthma and also as a decongestant. The consumption of *Ephedra* and *Achillea* leaves may pose a health risk of exposure to potentially toxic metals. Small grazing domestic animals are also in danger of excess exposure.

Even though so far no direct sign of health disorders was not observed, the arable soil in the vicinity of Dashkasan mining area needs further investigation assessing its suitability for agricultural use, particularly in view of the observed highly elevated concentrations of As, Hg and Pb. Regular monitoring is suggested to prevent future health problems.

**Acknowledgments** This research was financially supported by Medical Geology Research Center of Shiraz University to whom we are indebted. We would also like to extend our gratitude to Shiraz University research committee for logistical help. The authors are grateful to professor Khosravi for his help in plants identification.

## References

- Abrahams P, Thornton I (1987) Distribution and extent of land contaminated by arsenic and associated metals in mining regions



- of southwest England. Institution of Mining and Metallurgy. Transactions Section B. Applied Earth Science 96:1–8
- Adriano D (1986) Heavy metals in terrestrial environment. Springer, Berlin
- Alavi M, Vaziri H, Seyed-Emami K, Lasemi Y (1997) The Triassic and associated rocks of the Naxhlak and Aghdarband areas in central and northeastern Iran as remnants of the southern Turonian active continental margin. Geol Soc Am Bull 109:1563–1575
- Alloway B (1990) Soil processes and the behaviour of metals. In: Alloway B (ed) Heavy metals in soils, 2nd edn. Blackie Academic and Professional, London, pp 11–37
- Alloway BJ (2013) Bioavailability of elements in soil. In: Sellinus O (ed) Essentials of medical geology. Springer, New York, pp 351–373
- Alvarenga P, Araújo M, Silva J (2004) Elemental uptake and root-leaves transfer in *Cistus ladanifer* L. growing in a contaminated pyrite mining area (Aljustrel–Portugal). Water Air Soil Pollut 152:81–96
- Arakel AV, Hongjun T (1992) Heavy metal geochemistry and dispersion pattern in coastal sediments, soil, and water of Kedron Brook floodplain area, Brisbane, Australia. Environ Geol Water Sci 20:219–231
- Archer M, Caldwell R (2004) Response of six Australian plant species to heavy metal contamination at an abandoned mine site. Water Air Soil Pollut 157:257–267
- Aubert D, Probst A, Stille P (2004) Distribution and origin of major and trace elements (particularly REE, U and Th) into labile and residual phases in an acid soil profile (Vosges Mountains, France). Appl Geochem 19:899–916
- Batista M, Abreu M, Pinto MS (2007) Biogeochemistry in Neves corvo mining region, Iberian pyrite belt, Portugal. J Geochem Explor 92:159–176
- Berger B (1986) Descriptive model of epithermal quartz-alunite Au Mineral deposit models. US Geol Surv Bull 1693:158
- Biddau R, Cidu R (2005) Hydrogeochemical baseline studies prior to gold mining: a case study in Sardinia (Italy). J Geochem Explor 86:61–85
- Boccalletti M et al (1976) Neogene and Quaternary volcanism of the Bijar area (western Iran). Bull Volcanol 40:121–132
- Bolourchi M (1979) Explanatory text of the Kabudar-Ahang quadrangle map. Scale:1:250000. Geological Survey of Iran, Tehran
- Bowen HJM (1979) Environmental chemistry of the elements. Academic Press, Waltham, MA
- Bowles JE (1992) Engineering properties of soils and their measurement. McGraw-Hill Inc., New York
- Buat-Menard P (1979) Influence de la Retombée Atmosphérique sur la Chimie des Métaux en Trace dans la Matrice en Suspension de l'Atlantique Nord. Univ. Paris VI
- Cabri LJ, Newville M, Gordon RA, Crozier ED, Sutton SR, McMahon G, Jiang D-T (2000) Chemical speciation of gold in arsenopyrite. Can Mineral 38:1265–1281
- Chaney RL, Malik M, Li YM, Brown SL, Brewer EP, Angle JS, Baker AJ (1997) Phytoremediation of soil metals. Curr Opin Biotechnol 8:279–284
- Chen C-W, Kao C-M, Chen C-F, Dong C-D (2007) Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. Chemosphere 66:1431–1440
- Chopin E, Alloway B (2007) Distribution and mobility of trace elements in soils and vegetation around the mining and smelting areas of Tharsis, Riotinto and Huelva, Iberian Pyrite Belt, SW Spain. Water Air Soil Pollut 182:245–261
- Colbourn P, Alloway B, Thornton I (1975) Arsenic and heavy metals in soils associated with regional geochemical anomalies in south-west England. Sci Total Environ 4:359–363
- Cooke DR, Simmons SF (2000) Characteristics and genesis of epithermal gold deposits. Rev Econ Geol 13:221–244
- Craw D (2001) Tectonic controls on gold deposits and their environmental impact, New Zealand. J Geochem Explor 73:43–56
- Craw D, Chappell D, Reay A (2000) Environmental mercury and arsenic sources in fossil hydrothermal systems, Northland, New Zealand. Environ Geol 39(8):875–887
- Cui Y-J, Zhu Y-G, Zhai R-H, Chen D-Y, Huang Y-Z, Qiu Y, Liang J-Z (2004) Transfer of metals from soil to vegetables in an area near a smelter in Nanning, China. Environ Int 30:785–791
- Davies BE (1997) Deficiencies and toxicities of trace elements and micronutrients in tropical soils: limitations of knowledge and future research needs. Environ Toxicol Chem 16:75–83
- Del Rio M, Font R, Almela C, Vélez D, Montoro R, De Haro BA (2002) Heavy metals and arsenic uptake by wild vegetation in the Guadiamar river area after the toxic spill of the Aznalcóllar mine. J Biotechnol 98:125–137
- Dill HG (2010) The “chessboard” classification scheme of mineral deposits: mineralogy and geology from aluminum to zirconium. Earth Sci Rev 100:1–420
- Donkor A, Bonzongo J, Nartey V, Adotey D (2005) Heavy metals in sediments of the gold mining impacted Pra River basin, Ghana, West Africa. Soil Sediment Contam Int J 14:479–503
- Eby GN (2004) Principles of environmental geochemistry. Thomson-Brooks/Cole, Stamford
- Evans L, Spiers G, Zhao G (1995) Chemical aspects of heavy metal solubility with reference to sewage sludge amended soils. Int J Environ Anal Chem 59:291–302
- Fasani E (2012) Plants that hyperaccumulate heavy metals. Plants and heavy metals. Springer, Netherlands, pp 55–74
- Ferreira da Silva E, Zhang C, Li SP, Patinha C, Reis P (2004) Hazard assessment on arsenic and lead in soils of Castromil gold mining area, Portugal. Appl Geochem 19:887–898
- Folk RL (1980) Petrology of sedimentary rocks. Hemphill Publishing Co, Texas
- Gal J, Hursthouse A, Cuthbert S (2007) Bioavailability of arsenic and antimony in soils from an abandoned mining area, Glendinning (SW Scotland). J Environ Sci Health Part A 42:1263–1274
- Getaneh W, Alemayehu T (2006) Metal contamination of the environment by placer and primary gold mining in the Adola region of southern Ethiopia. Environ Geol 50:339–352
- Ghorbani M (2013) The economic geology of Iran, mineral deposits and natural resources. Springer, New York
- Greger M (1999) Metal availability and bioconcentration in plants. In: Prasad MN, Hagemeyer J (eds) Heavy metal stress in plants. Springer, Berlin, pp 1–27
- Guillén MT, Delgado J, Albanese S, Nieto JM, Lima A, De Vivo B (2012) Heavy metals fractionation and multivariate statistical techniques to evaluate the environmental risk in soils of Huelva Township (SW Iberian Peninsula). J Geochem Explor 119:32–43
- Hakanson L (1980) An ecological risk index for aquatic pollution control: a sedimentological approach. Water Res 14:975–1001
- Hayba DO, Bethke PM, Heald P, Foley NK (1985) Geologic, mineralogic, and geochemical characteristics of volcanic-hosted epithermal precious-metal deposits. Rev Econ Geol 2:129–167
- He M, Yang J (1999) Effects of different forms of antimony on rice during the period of germination and growth and antimony concentration in rice tissue. Sci Total Environ 243:149–155
- Hedenquist JW, Arribas A, Gonzalez-Urien E (2000) Exploration for epithermal gold deposits. Rev Econ Geol 13:245–277
- Henley R (1991) Epithermal gold deposits in volcanic terranes. Gold metallogeny and exploration. Springer, New York, pp 133–164
- Hernandez L, Probst A, Probst JL, Ulrich E (2003) Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. Sci Total Environ 312:195–219

- Imperato M, Adamo P, Naimo D, Arienzo M, Stanzione D, Violante P (2003) Spatial distribution of heavy metals in urban soils of Naples city (Italy). *Environ Pollut* 124:247–256
- Jung MC, Thornton I (1996) Heavy metal contamination of soils and plants in the vicinity of a lead–zinc mine. *Korea Appl Geochem* 11:53–59
- Kabata-Pendias A, Pendias H (1992) Trace elements in soils and plants. CRC Press, Michigan, pp 365
- Kabata A, Pendias H (2001) Trace elements in soils and plants. CRC, New York
- Kabata-Pendias A (2011) Trace elements in soils and plants, 4th edn. Taylor and Francis Group, LLC, Florida
- Kabata-Pendias A, Mukherjee AB (2007) Trace elements from soil to human. Springer, New York
- Kachenko AG, Singh B (2006) Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia. *Water Air Soil Pollut* 169:101–123
- Kloke A, Sauerbeck D, Vetter H (1984) The contamination of plants and soils with heavy metals and the transport of metals in terrestrial food chains. Changing metal cycles and human health. Springer, New York, pp 113–141
- Koljonen T (1992) The geochemical atlas of Finland. Espoo, Finland
- Kurdistan Meteorological Organization (2013) Annual internal report. Kurdistan Meteorological Organization Web. <http://www.kurdistanmet.ir/viewStatistic.aspx>. Accessed 2 Sept 2013
- Lakin HW (1974) Geochemistry of gold in the weathering cycle. *US Geol Surv Bull* 1330:80
- Lescuyer J, Hushmand Zadeh A, Daliran F (2003) Gold metallogeny in Iran: a preliminary review Mineral exploration and sustainable development, 2nd edn. Mill Press, Rotterdam, pp 1185–1188
- Levinson AA (1980) Introduction to exploration geochemistry. Applied Publishing Co, Wilmette, pp 924
- Lokeshwari H, Chandrappa G (2006) Impact of heavy metal contamination of Bellandur Lake on soil and cultivated vegetation. *Curr Sci* 91:622–627
- Loska K, Wiechula D, Barska B, Cebula E, Chojnecka A (2003) Assessment of arsenic enrichment of cultivated soils in Southern Poland. *Polish J Environ Stud* 12:187–192
- Lottemoser B (1995) Alteration of noble metals in municipal sewage sludges of Southern Australia. *Ambio* 24:354–357
- Lu S, Bai S (2010) Contamination and potential mobility assessment of heavy metals in urban soils of Hangzhou, China: relationship with different land uses. *Environ Earth Sci* 60:1481–1490
- Madejón P, Lepp NW (2007) Arsenic in soils and plants of woodland regenerated on an arsenic-contaminated substrate: a sustainable natural remediation? *Sci Total Environ* 379:256–262
- Maestri E, Marmiroli M, Visioli G, Marmiroli N (2010) Metal tolerance and hyperaccumulation: costs and trade-offs between traits and environment. *Environ Exp Bot* 68(1):1–13
- Martínez-Sánchez M, Pérez-Sirvent C, Molina J, Tudela M, Navarro M, García-Lorenzo M (2009) Heavy metal pollution in soils of abandoned mining areas (SE, Spain). *Geophys Res Abstract* 11:3788
- McBride MB (1994) Environmental chemistry of soils. Oxford University Press, Oxford
- Moore F, Dehghani S, Keshavarzi B (2014) Characterization of soil contamination in Miduk mining district, SW Iran. *Soil Sediment Contam Int J* 23:614–627
- Moritz R, Ghazban F, Singer BS (2006) Eocene gold ore formation at Muteh, Sanandaj-Sirjan tectonic zone, Western Iran: a result of late-stage extension and exhumation of metamorphic basement rocks within the Zagros Orogen. *Econ Geol* 101:1497–1524
- Mountain B, Seward T (2003) Hydrosulfide/sulfide complexes of copper (I): experimental confirmation of the stoichiometry and stability of Cu (HS) 2– to elevated temperatures. *Geochim Cosmochim Acta* 67:3005–3014
- Navarro M, Pérez-Sirvent C, Martínez-Sánchez M, Vidal J, Tovar P, Bech J (2008) Abandoned mine sites as a source of contamination by heavy metals: a case study in a semi-arid zone. *J Geochem Explor* 96:183–193
- Niroomand S, Rastad E, Rashid Nejad-Emran N, Ghaderi M (2013) Geology and ore mineralogy of Dashkasan (Sari Gunay) epithermal gold deposit in Sanandaj-Sirjan Belt, Eastern Ghorveh, Kordestan Province Geosciences: Iranian scientific. *Q J* 88:30–41 (In Farsi with English abstract)
- NRC (1977) Arsenic: medical and biological effects of environmental pollutants. Committee on Medical and Biological Effects of Environmental Pollutants, National Academies Press, Washington
- Nriagu J (ed) (1978) Biogeochemistry of lead in the environment, part 1. Ecological cycles vol 1A. Elsevier, Amsterdam
- Ogola JS, Mitullah WV, Omulo MA (2002) Impact of gold mining on the environment and human health: a case study in the Migori gold belt. *Kenya Environ Geochem Health* 24:141–157
- Oyarzun R, Lillo J, Higuera P, Oyarzún J, Maturana H (2004) Strong arsenic enrichment in sediments from the Elqui watershed, Northern Chile: industrial (gold mining at El Indio-Tambo district) vs. geologic processes. *J Geochem Explor* 84:53–64
- Pais I, Jones JB (1997) The handbook of trace elements. CRC Press, Florida
- Pekey H (2006) Heavy metal pollution assessment in sediments of the Izmit Bay. *Turk Environ Monit Assess* 123:219–231
- Plumlee GS, Gray J, Roeber Jr M, Coolbaugh M, Flohr M, Whitney G (1995a) The importance of geology in understanding and remediating environmental problems at Summitville. In: Proceedings: summitville forum, pp 13–22
- Plumlee GS, Smith KS, Berger BR, Foley-Ayuso N, Klein DP (1995b) Creede, Comstock, and Sado epithermal vein deposits preliminary compilation of descriptive geoenvironmental mineral deposit models. In: du Bray E (ed) Open file report OFR-95-0831, US Geological Survey, Denver, CO, pp 152–161
- Rafiei B, Bakhtiari Nejad M, Hashemi M, Khodaei A (2010) Distribution of heavy metals around the Dashkasan Au mine. *Int J Environ Res* 4:647–654
- Rastad E, Niroomand S, Emami M, Rashid Nejad-Emran N (2000) Genesis of Sb–As–Au deposit in volcanoplautonic complex of Dash-kasan (East Qorveh, Kordestan Province). *Geosci: Iranian Sci Q J* 9:2–9 (In Farsi with English abstract)
- Razo I, Carrizales L, Castro J, Díaz-Barriga F, Monroy M (2004) Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico. *Water Air Soil Pollut* 152:129–152
- Richards JP, Wilkinson D, Ullrich T (2006) Geology of the Sari Gunay epithermal gold deposit, northwest Iran. *Econ Geol* 101:1455–1496
- Rizzi L, Petruzzelli G, Poggio G, Guidi GV (2004) Soil physical changes and plant availability of Zn and Pb in a treatability test of phytostabilization. *Chemosphere* 57:1039–1046
- Robb L (2005) Introduction to ore-forming processes. Wiley, New York
- Ronacher E, Richards J, Reed M, Bray C, Spooner E, Adams P (2004) Characteristics and evolution of the hydrothermal fluid in the North zone high-grade area, Porgera gold deposit, Papua New Guinea. *Econ Geol* 99:843–867
- Rotkittikhun P, Kruatrachue M, Chaiyarat R, Ngernsarsaruy C, Pokethitiyook P, Pajitprapaporn A, Baker A (2006) Uptake and accumulation of lead by plants from the Bo Ngam lead mine area in Thailand. *Environ Pollut* 144:681–688
- Sayyareh A, Fonoudi M, Dadsetan A (2005) Environmental geology study in Qorveh-Bijar area. Geological and Environmental management Group Preliminary report. Geological Survey of Iran, Tehran

- Sheppard SC, Sheppard MI, Gallerand MO, Sanipelli B (2005) Derivation of ecotoxicity thresholds for uranium. *J Environ Radioact* 79(55):83
- Singh J, Upadhyay SK, Pathak PK, Gupta V (2011) Accumulation of heavy metals in soil and paddy crops (*Oryza sativa*), irrigated with water of Ramgrah Lake, Gorakhpur, UP, India. *Toxicol Environ Chem* 93(3):462–473
- Smeyers-Verbeke J, Graeve M, Francois M, Jaeger R, Massart D (1978) Cd uptake by intact wheat plants. *Plant Cell Environ* 1:291–296
- Smith K, Moiser E, Montour M, Plumlee G, Ficklin W, Briggs P, Meier A (1995) Yearly and seasonal variations in acidity and metal content of irrigation waters from the Alamosa River, Colorado. In: *Proceedings summitville forum '95*, Colorado Geological Survey Special Publication, 1995. pp 293–298
- Stefánsson A, Seward T (2004) Gold (I) complexing in aqueous sulphide solutions to 500 °C at 500 bar. *Geochim Cosmochim Acta* 68:4121–4143
- Stocklin J (1968) Structural history and tectonics of Iran: a review. *AAPG Bull* 52:1229–1258
- Tarnocai C, Hattori K, Cabri L (1997) Invisible gold in sulfides from Campbell mine, Red lake greenstone belt, Ontario: evidence for mineralization during the peak of metamorphism. *Can Mineral* 35:805–815
- Tomlinson D, Wilson J, Harris C, Jeffrey D (1980) Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index. *Helgoländer Meeresuntersuchungen* 33:566–575
- Tumuklu A, Yalcin MG, Sonmez M (2007) Detection of heavy metal concentrations in soil caused by Nigde City Garbage Dump, Poland. *J Environ Stud* 16:651–658
- Vernadsky V (1997) *The biosphere, copernicus*. Springer, New York
- Wedepohl KH (1986) *Handbook of geochemistry*. Springer, Berlin
- Wilkinson D, Bartran J (2003) *Geology and mineralogy of the Dashkasanold deposit, Kordestan province, Iran*. Rio Tinto Exploration, Salt Lake City
- Zhang H, Luo Y, Wong M, Zhao Q, Zhang G (2007a) Defining the geochemical baseline: a case of Hong Kong soils. *Environ Geol* 52:843–851
- Zhang L et al (2007b) Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China. *Mar Pollut Bull* 54:974–982
- Zheng Y, Gao Q, Wen X, Yang M, Chen H, Wu Z, Lin X (2013) Multivariate statistical analysis of heavy metals in foliage dust near pedestrian bridges in Guangzhou, South China in 2009. *Environ Earth Sci* 70:107–113
- Zhu Y, An F, Tan J (2011) Geochemistry of hydrothermal gold deposits: a review. *Geosci Front* 2:367–374
- Zhuang P, McBride MB, Xia H, Li N, Li Z (2009) Health risk from heavy metals via consumption of food crops in the vicinity of Dabaoshan mine, South China. *Sci Total Environ* 407:1551–1561