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ORIGINAL PAPER

Arsenic in soil and vegetation of a contaminated area

N. Karimi · S. M. Ghaderian · H. Schat

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Abstract Plant and soil samples were collected from one uncontaminated and four contaminated sites (in the Dashkasan mining area western Iran). Total and water-soluble arsenic in the soil ranged from 7 to 795 and from 0.007 to 2.32 mg/kg, respectively. The highest arsenic concentration in soil was found at the ore dressing area (up to 1,180 mg/kg) and lowest at an uncontaminated area (up to 11 mg/kg). A total of 49 plant species belonging to 15 families were collected from four sampling sites. A significant positive correlation was detected between the concentrations of arsenic in plant dry matter and those in soils. The highest arsenic concentrations were found in *Hyoscyamus kurdicus* Bornm. (up to 205 mg/kg) and *Helichrysum oligocephalum* DC. (up to 162 mg/kg). These two accumulator species could have potential for soil clean-up by phytoextraction. The data have been compared with those for the Zarshuran mining area (north-western Iran) obtained in a former study.

Keywords Bioavailability · Contamination · Phytoremediation · Plant

N. Karimi (✉)
Laboratory of Plant Physiology, Department of Biology, Faculty of Science, Razi University, Kermanshah, Iran
e-mail: nkarimie@yahoo.com

S. M. Ghaderian
Laboratory of Plant Physiology, Department of Biology, Faculty of Science, Isfahan University, Isfahan, Iran

H. Schat
Department of Genetics, Faculty of Earth and Life Sciences, Vrije Universiteit, de Boelelaan 1085, 1081 HV Amsterdam, The Netherlands

Introduction

Arsenic (As) is a widely distributed environmental pollutant, with toxic effects on plants. Arsenic contamination in soils originates from various anthropogenic sources, such as mining, milling, and agricultural applications, as well as natural geochemical processes (Smith et al. 2002; Welch 2002). Mining activities may cause heavy local and regional As pollution of soils and waters, for example, mine tailings may contain As up to several thousands of mg/kg, although the crustal average is only 2 mg/kg (Boyle and Jonasson 1973). Mining activities cause the degradation of agricultural, pasture, or forest land, with a concomitant reduction in the biomass productivity and biodiversity, which directly affects economic wealth (Wong 2003). Moreover, high As concentrations in soils are directly reflected in crops, and are one of the major sources of As in drinking water (Zhang et al. 2002; Reza and Singh 2010).

Human beings and domestic animals are exposed to As via different pathways. Among them, drinking water is the main route of As intake into the human body. The food chain can also be significant route of As uptake into the human body, when people are consuming As-contaminated cereals, vegetables, or animals (Anawar et al. 2006). The study of As uptake by plants is significant in three ways: (1) it provides an indication of the bioavailable fraction of the soil As (dependent on plant species), and (2) of a plant species' potential for phytoremediation, and (3) of the amount of As that is potentially available to herbivores (Casado et al. 2007).

The current technologies for the remediation of metal/metalloid-contaminated soils are expensive, time consuming, and can create risks to workers, or produce secondary waste (Wenzel et al. 1999; Lombi et al. 2000; Pratas et al. 2005). Recently, phytoremediation has been proposed as a

cost-effective, promising and environment friendly alternative (McGrath et al. 1993; Baker 1995). Phytoremediation uses plants to prevent the spread of contaminants via wind, run-off, or groundwater ('phytostabilization'), or to extract them from the soil and remove them from the system through harvest of the aboveground plant biomass ('phyto-extraction'). Plant species that grow fast, produce high biomass and accumulate large amounts of As from the soil are promising candidates to phytoremediate the As-contaminated land in the mining areas (Anawar et al. 2006). In addition, for an effective phyto-extraction process, it is essential to enhance the pollutant phytoavailability, and to sustain adequate pollutant concentrations in the soil solution for plant uptake (Lombi et al. 2000). A major step towards the development of phytoremediation of As-impacted soils is the discovery of the As-hyperaccumulating pteriod ferns, among which the well-known *Pteris vittata* (Zhao et al. 2009). These plants produce large biomass and are therefore promising candidates for phyto-extraction purposes (Ma et al. 2001; Francesconi et al. 2002).

It is often difficult to predict the behavior and fate of As in a contaminated matrix exclusively through extrapolating results obtained from laboratory ecotoxicity experiments (Gulz et al. 2005). Local circumstances can have profound effects. We previously conducted a study in the Zarshuran area (north-western Iran), which has a long history of As pollution through mining (Modabberi and Moore 2004; Karimi et al. 2010). Total and water-soluble As in the soil and their relationship with plant uptake were investigated. Over a broad range of soil As concentrations, *Isatis cappadocica* and *Hesperis persica* maintained more than tenfold higher foliar As concentrations and soil to leaf As transfer coefficients, in comparison with all the other species sampled at the same sites. Therefore, they were classified as the first angiosperm As hyperaccumulators. Because As uptake and accumulation from soils by plants are influenced by factors such as plant species (Matschullat et al. 2000), soil arsenic concentration (Jiang and Singh 1994), and other chemical and physical soil properties, among which the concentrations of other ions, particularly phosphate (Khattak et al. 1991; Jiang and Singh 1994; Matschullat et al. 2000), or the age of the plants, comparing the Zarshuran and Dashkasan data sets would be very useful, possibly providing confirmatory evidence, or new insights.

The Dashkasan antimony–arsenic–gold deposit, located in the Kurdistan province, western Iran, is one of the most important antimony producing areas in Iran. Antimony production is associated with elevated environmental concentrations of As, gold and antimony (Moritz et al. 2006). This contamination originates from As-rich waste disposed both by mining and smelting operations carried out in this area (Lescuyer et al. 2003). Dashkasan has a relatively rich plant biodiversity, and there is no information on the bioaccumulation potential of plant species indigenous to this area, hence there are possibilities to encounter locally adapted species with favorable properties for the phytoremediation of As-contaminated land.

Therefore, the objectives of this study were to (1) determine As concentrations in plants and soils, (2) establish the bioavailable As fractions of soils, and (3) determine the bioaccumulation of As in the wild plant species of the Dashkasan mining area, to assess their phytoextraction potentials, and compare these with those of the plants from the Zarshuran area (Karimi et al. 2010). To this purpose, soil and plant samples located in As-contaminated areas in the Dashkasan deposit were taken in the period from May to September, 2009.

Materials and methods

Study area

Dashkasan is an antimony–arsenic–gold deposit located at 35°14′N 48°7′E, 42 km NE of Qorveh city in the Kurdistan province, western Iran (Fig. 1). The area is a part of the Sanandaj–Sirjan magmatic–metamorphic zone (Moritz et al. 2006). The deposit is defined as a sulfide-silicic vein deposit, mineralized by tectonic structures (Rastad et al. 2002). The deposit is hosted by dacite, rhyodacite and microgranodiorite subvolcanic rocks, which are mainly associated with silicic, argillic, and pyritic alteration. Mining activities produced huge amounts of wastes, among which fine-grained ore minerals including arsenopyrite, and ore weathering products (Fe-oxyhydroxides, sulfates and scorodite) (Lescuyer et al. 2003). The mineral paragenesis consists of quartz, stibnite, pyrite, realgar, orpiment, pyrrhotit, chalcopyrite, bornite, galena, boulangerite, gold, stibiconite, kermesite and iron hydroxide (Rafiei et al. 2010).

Sampling

Plants and soil samples were collected from different locations during the period of May till September 2009: site 1 (control) is located 10 km away from mine to the east, site 2 (Dashkasan-T1) is located near an ancient main open pit 1 km to the north of site 1, site 3 (Dashkasan-T2) corresponds to a minor open pit and waste dump situated 1 km to the east of site 1, and site 4 (Zarnikh) is located around the main waste dump. A total of 17 soil samples were collected from (0–10 cm). A total of 78 plant samples belonging to 49 different species were collected. Only the aerial parts of the plant (stems, branches and leaves) were collected.

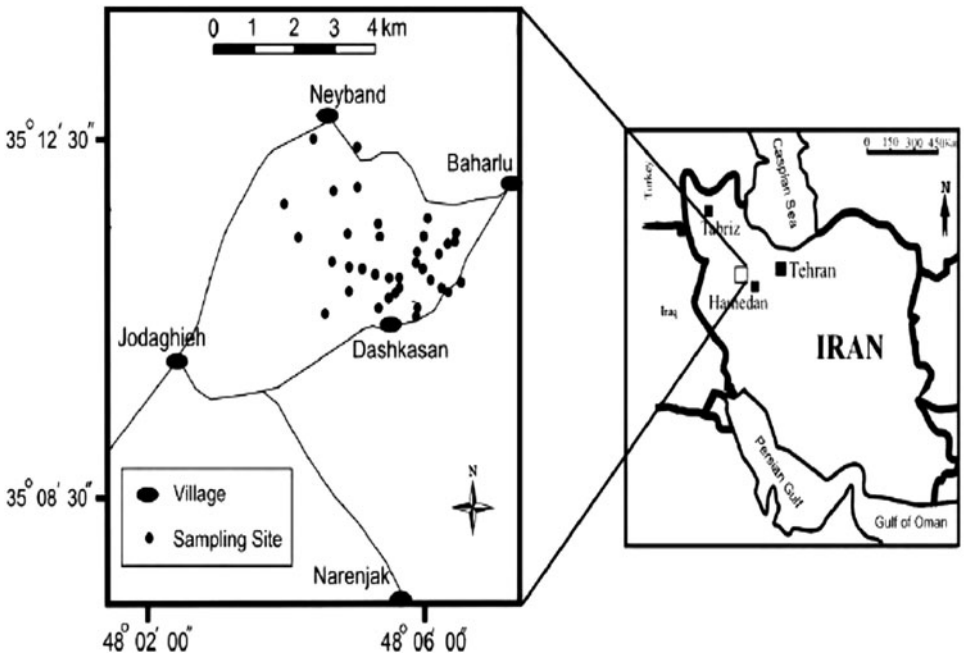

Fig. 1 Location of the study area and sampling sites at the Dashkasan deposit in Iran

Soil characteristics

The soil samples were dried at 50 °C, mixed, homogenized and sieved through a 2-mm grid. Soil properties were determined as follows: pH was determined potentiometrically in a soil paste saturated with water; organic matter was determined by dichromate oxidation using the Tiurin method (Soon and Abboud 1991); cation exchange capacity (CEC) was determined according to the ammonium acetate method by extracting with a 1.0 mol/l NH_4OAc solution (pH 7.0); and particle size distribution (sand, silt, and clay) was analyzed by the pipette method (Ashworth et al. 2001).

Analysis of As in plant samples

Plant samples were cleaned with fresh-water, rinsed with deionized water and oven-dried at 70 °C to constant weight. The oven-dried plant samples were powdered in a stainless-steel mill to obtain a homogeneous sample and prepared for analysis. They were digested as described by Meharg and Jardine (2003). The ground plant samples (0.5 g) were placed in a digestion tube and mixed with 2.5 ml of concentrated nitric acid. The digest was allowed to stand overnight and then 2.5 ml of concentrated H_2O_2 was added. The tubes were placed on a digestion block and heated at 100 °C until frothing stopped, then heated at 140 °C until the solutions became clear. The tubes were then heated to 180 °C to boil off the nitric acid. On cooling, the residue was taken up in 10 ml of a solution containing 10 % HCl, 5 % ascorbic acid and 10 % KI. Arsenic concentrations were measured in duplicate using a Shimadzu spectra AA-6200 Atomic Absorption Spectrophotometer with a hydride generator (WHG 103A).

Standard materials for chemical analysis were purchased from Merck and the calibration curve fit (at least five standard concentrations) was with $R^2 > 0.97$ in all cases. The method's recovery of As (0.79 ± 0.08 mg/kg) from certified reference material (Beach leaves material FD8, Commission of the European Communities, Joint Research Centre ISPRA) was not significantly different from the certified reference value (0.76 ± 0.1 mg/kg). The mean As concentration in blank digests was 0.08 µg/l and the detection limit for As in plant digests was 0.05 µg/l.

Analysis of As in soil samples

The finely powdered and homogenized soil samples (0.5 g) were digested with 10 ml of a 3:1 HCl/HNO_3 mixture in a Kjeldahl digestion tube. Tubes were left overnight at room temperature and then placed in a heating block. Each was covered with an air condenser and refluxed gently at 80 °C for 2 h. After cooling, the digests were filtered through a moistened Whatman No. 40 filter paper into a 50 ml volumetric flask and 10 ml of a solution containing 10 % HCl, 5 % ascorbic acid and 10 % KI was added. Flasks were then made up to volume with distilled water. Analysis of As was performed by atomic absorption spectrophotometry, as described above.

Water-soluble arsenic

Water-soluble As was measured as described by Anawar et al. (2006). Soil and Milli-Q water were mixed in 1:10

proportion and the mixed solution was shaken for 24 h using a rotary shaker. The solution was centrifuged at 3,000 rpm; and then the supernatant was collected and filtered. Arsenic in the filtered solution was measured by the HG-AAS method described above.

Results and discussion

Soil characteristics

The pH, organic matter (OM), CEC and soil texture of each site, together with the total and soluble As concentrations, are given in Table 1. The pH values ranged from 5.4 to 6.5, comparable with the range for the Zarshuran area (Table 1). The contents of organic matter ranged from 2.52 to 5.85 % with a mean value of 3.5 %, which is high, in comparison with the Zarshuran area. These higher organic matter contents in the soils are possibly due to the dense vegetation cover, which was lacking in the Zarshuran area. The CEC varied from 5.9 to 14.3 meq/100 g with a mean value of 8.7 meq/100 g in study sites (Table 1). The CEC of the soils at site 4 (12.80–16.53) demonstrated a high acid buffering capacity, while the CEC values at sites 1, 2 and 3 showed a low acid buffering capacity. The soil texture analysis revealed significant differences between sites, particularly with regard to the sand and clay fractions. At site 4, the content of sand was much higher than that of clay, whereas the opposite pattern was found at site 2 (Table 1).

It is generally known that rhizosphere pH may considerably differ from that in the bulk soil.

Depending on the plant and soil factors pH differences can be up to two units. Factors affecting rhizosphere pH are the source of nitrogen (NO_3^- versus NH_4^+ uptake), nutritional status of (e.g. Fe and P deficiency), excretion of organic acids, CO_2 production by roots and rhizosphere microorganisms, as well as the buffering capacity of the soil. Under aerobic conditions As is mainly present as As^V, which is desorbed from adsorption sites upon pH increase. Both plant-induced decreases of the redox potential (e^-) and drastic pH decreases in the rhizosphere may dissolve Fe oxides/hydroxides, resulting in the concomitant release of As and P into the soil solution.

Redox potential and pH control the prevailing redox- and hydrolysis-status of As in the soil solution. Carboxylic acids (R-COOH) released by P deficient plants have been reported to be involved in the mobilisation of inorganic P in the rhizosphere (Neumann and Römheld 1999; Kirk et al. 1999; Dinkelaker et al. 1995). Such processes are also likely to affect As availability, due to the well-known physico-chemical similarities between arsenate and phosphate, resulting in competition for sorption sites in soil (Adriano 2001), and for plant uptake via high-affinity P

Table 1 Mean (range) of total and water-soluble arsenic concentrations (mg/kg) and physico-chemical characteristics of Dashkasan mine soil

Sampling site	AS (total)	AS (soluble)	Organic matter (wt%)	pH	Silt (%)	Clay (%)	Sand (%)	CEC (meq/100 g)
S1 (uncontaminated site; $n = 4$)	7 (4–11)	0.007 (0.003–0.007)	4.31 (3.8–5.3)	6.8 (6.3–6.9)	15	31	36	6.5 (5.3–7.1)
S2 ($n = 3$)	125 (85–186)	0.08 (0.03–0.09)	3.42 (2.7–4.6)	6.2 (5.9–6.4)	23	45	33	5.9 (5.5–7.3)
S3 ($n = 5$)	426 (375–561)	0.9 (0.5–0.8)	2.52 (1.9–3.3)	6.4 (5.9–6.8)	36	21	35	8.7 (8.3–9.1)
S4 ($n = 5$)	795 (720–1,180)	2.32 (1.26–3.25)	5.85 (5.18–6.41)	5.8 (5.4–6.1)	32	18	49	14.3 (12.8–16.5)

transporters (Asher and Reay 1979). In acid soils, iron and aluminum oxides are the primary sorbents of arsenate, which is the predominant As species in agricultural soils (Marin et al. 1993; Pongratz 1998). In alkaline soils, arsenate is sorbed by calcium oxides, but this adsorption is less intense than that at lower pH on iron and aluminum oxides (Woolson et al. 1971).

Arsenic in soil

The mean total As concentration in the soil ranged from 4 mg/kg at the uncontaminated site 1 (S1) to 719 mg/kg at site 4 (S4). The soil of site 4 contained the highest As concentrations and was affected to a great extent by mine tailings and spoils. The mean As concentration overall the sites (except for site 1) in this study was higher than the average toxicity threshold of 40 mg/kg established for agricultural soil (Sheppard 1992). Mining is the most important emission source of As to the environment in this area. Arsenic may originate mainly from the mechanical dispersion of arsenopyrite mineral around the mine tailings, and/or the variable degree of weathering of these minerals.

In comparison with our previous study (Zarshuran area), the soil samples in the Dashkasan area had lower total As concentrations. However, the water-soluble fractions of soil As were much higher in the Dashkasan area than in the Zarshuran one (Fig. 2).

Water-soluble As is considered to be a good estimate of the bioavailable fraction and the risk level of As contamination in soils (Casado et al. 2007). At site 4, the water-soluble As concentration (1.41–5.92 mg/kg) was much higher than at site 2 (0.03 mg/kg) and site 3 (1.7 mg/kg, Table 1). Except for the uncontaminated site (S1) and site S2, the water-soluble As concentrations exceeded the maximum permissible level of 0.04 mg/kg for agricultural soils, indicating the enriched bioavailability of As for plants growing in this area (Bohn et al. 1985).

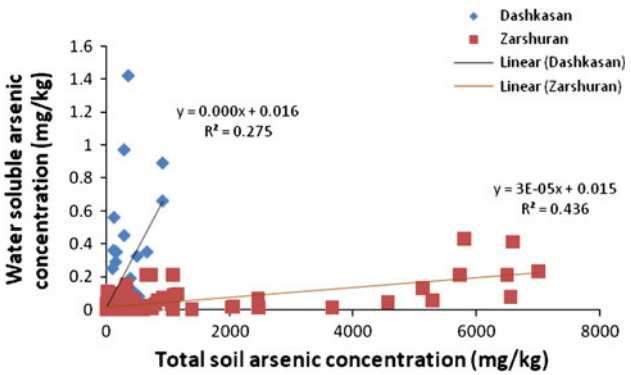

Fig. 2 Total soil arsenic concentration plotted against soil water soluble As concentrations for samples from four sites of the Dashkasan deposit in Iran

In some samples (4 out of 10) the water-soluble As fractions were higher (0.44, 0.56, 0.71 and 0.78 % of total As) than in others and those reported by Kavanagh et al. (1997) and Casado et al. (2007). In comparison with Xu and Thornton (1985) and Cao and Ma (2004), reporting maximum water-soluble As fractions of 2.78 and 3.02–13.6 % in garden soils in Cornwall and contaminated soils in the USA, respectively, the values obtained in the Dashkasan area were very low, probably due to the relatively low organic matter content.

The soil organic matter content was correlated with water-soluble soil As ($r = 0.54$, $p < 0.01$), probably because humic or fulvic acids are blocking adsorption sites of amorphous soil colloids, thus enhancing As solubility (Casado et al. 2007). This can be explained by the anionic nature of many organic compounds in soil, resulting in reduced As adsorption on Al and Fe oxides/hydroxides. In this respect it is important that arsenate is present in the anionic form, thus competing with the negatively charged humic and fulvic acid residues for binding sites at Al or Fe oxides/hydroxides. As expected, the relatively high As water solubility at the S3 and S4 sites coincided with relatively high organic matter contents and cation-exchange capacities.

Arsenic in plants

A total of 49 plant species of vascular plants were sampled from different sites in the Dashkasan mining area (Table 2). The species were mostly Asteraceae (10), Lamiaceae (9), Fabaceae (6) and Scrophulariaceae (4). Most of the plants are herbaceous perennials. There are no trees and only a few shrubs among them.

There was a broad variation of mean As concentrations among plant species, ranging from 0.2 to 139 mg/kg (Table 2). The plant species at site 1 (uncontaminated site) showed very low arsenic concentrations (Table 2). The mean As concentrations at site 4 were the highest (ranging from 14 to 139 mg/kg). Only in two species, *Helichrysum oligocephalum* DC. (113 mg/kg) and *Hyoscyamus kurdicus* Bornm. (139 mg/kg), the As concentration exceeded 100 mg/kg (Table 2). A part from *H. oligocephalum* and *H. kurdicus*, also *Nonea persica* and *Salvia syriaca* accumulated relatively high As concentrations in their shoots at this site (Table 2). On the other hand, *Astragalus gossypinus* (8.3 mg/kg), *Achillea biebersteinii* (8.2 mg/kg) and *Lepidium persicum* (28 mg/kg) exhibited very low As concentrations, although they were growing in strongly As-enriched soil. In most of the plants studied here the As concentrations were higher than the background concentrations in plants from pristine environments [non-detectable to 3 mg/kg dry weight (Koch et al. 2000)]. Much higher As concentrations were found in several plants from

Table 2 Mean (range) shoots arsenic concentrations (mg/kg) and arsenic transfer coefficient (AsTC) in plant species growing at uncontaminated (S1) and contaminated (S2–S4) sites

Family	Name	Site	Type	Mean AsTC	Mean As concentration (ppm)
Apiaceae	*Eryngium* sp.	1	Forb	0.038	0.2
Apiaceae	*Prangos latiloba* Korov.	1	Forb	0.064	0.3
Asteraceae	*Cousinia* sp.	2	Forb	0.089	11
Asteraceae	*Achillea biebersteinii* ($n = 3$)	2, 4	Forb	0.053 (0.041–0.064)	8.2 (5–9.8)
Asteraceae	*Senecio vulgaris* L.	3	Forb	0.07	29.3
Asteraceae	*Pedophyllom* sp.	3	Forb	0.112	35
Asteraceae	*Centaurea depressa* M.B.	2	Forb	0.039	3.8
Asteraceae	*Causinia* sp.	1	Forb	0.048	1.8
Asteraceae	*Helichrysum oligocephalum* DC. ($n = 7$)	4	Forb	0.10 (0.08–0.12)	113 (85–162)
Asteraceae	*Tanacetum polycephalum* Schultz-Bip	*3*	Forb	0.025	9.8
Asteraceae	*Centaurea* sp.	*4*	Forb	0.051	6.4
Asteraceae	*Centaurea behen* L.	*2*	Forb	0.025	12.6
Boraginaceae	*Nonea persica* Boiss.	4	Forb	0.071	65
Boraginaceae	*Alkanna orientalis* L.	*2*, *3*	Forb	0.047	0.5
Brassicaceae	*Lepidium persicum* Boiss. subsp. *persicum*	4	Forb	0.053	28
Brassicaceae	*Fibigia suffruticosa* (Vent.) Sweet	1	Forb	0.025	0.21
Brassicaceae	*Alyssum stapfii* Vierh. ($n = 2$)	3	Forb	0.018	0.2 (0–0.31)
Brassicaceae	*Cardaria draba* (L.) Desv. ($n = 4$)		Forb	0.103 (0.09–0.12)	14.8 (9.7–17)
Caryophyllaceae	*Acanthophyllum squarrosum* Boiss.	2	Shrub	0.055	4.8
Dipsacaceae	*Pterocephalus canus* Coult. DC.	2	Forb	0.087	8.7
Euphorbiaceae	*Euphorbia heteradena* Jaub. & Sp.	1	Forb	0.012	0.3
Fabaceae	*Astragalus* sp.	2	Shrub	0.055	4.32
Fabaceae	*Astragalus vegetus* Bunge	3	Forb	0.075	35
Fabaceae	*Astragalus chrysanthus*	1	Shrub	0.026	0.15
Fabaceae	*Astragalus gossypinus* Fischer ($n = 5$)	4	Forb	0.044	8.36
Fabaceae	*Sophora alopecuroides* L.	1	Shrub	0.004 (0.002–0.007)	0.25 (01–0.31)
Fabaceae	*Medicago sativa* L.	1	Forb	0.066	33.3
Lamiaceae	*Lagochilus aucheri* Boiss.	2	Forb	0.039	0.3
Lamiaceae	*Salvia* sp.	4	Forb	0.101	6
Lamiaceae	*Salvia hypoleuca* Benth.	*2*	Forb	0.073	21.3
Lamiaceae	*Lagochilus aucheri* Boiss.	1	Forb	0.081	17.5
Lamiaceae	*Stachys inflate* Benth.	2	Forb	0.048	6.53
Lamiaceae	*Phlomis olivieri* Benth.	3, 4	Forb	0.063	5.65
Lamiaceae	*Stachys lavandulifolia* Vahl ($n = 3$)	1, 2	Forb	0.085 (0.067–0.093)	78.53 (65–98)
Lamiaceae	*Thymus migricus* Klokov & Desj.-Shost.	1	Forb	0.071	25.65
Lamiaceae	*Salvia syriaca* L. ($n = 3$)	3, 4	Forb	0.035 (0.017–0.053)	5.53 (3.50–8)

Table 2 continued

Family	Name	Site	Type	Mean AsTC	Mean As concentration (ppm)
Plantaginaceae	*Plantago lanceolata* L. ($n = 5$)	3, 4	Forb	0.66 (0.04–0.081)	29.6 (19–41.1)
Papaveraceae	*Papaver* sp.	1	Forb	0.032	1.1 1
Poaceae	*Triticum aestivum* L. emend. Fiori & Paol. ($n = 3$)	2, 3	Forb	0.094 (0.071–0.12)	9.3 (1.2–5.5)
Poaceae	*Eremopyrum distans* (C. Koch) Nevski	4	Grass	0.072	18.63
Poaceae	*Boissiera squarrosa* (Banks & Soland.) Nevski	2	Forb	0.092	9.4
Rosaceae	*Rosa persica* Michx. Ex Juss.	*3*	Shrub	0.011	7.3
Rubiaceae	*Cruci iataurica* (Pallasex Willd)	*1*	Forb	0.017	7.2
Scrophulariaceae	*Verbascum pseudo-digitalis* Nab.	2	Forb	0.041	0.23
Scrophulariaceae	*Linaria* sp.	1	Forb	0.004	0.8
Scrophulariaceae	*Linaria kurdica* Boiss. et Hoh.	2	Forb	0.083	0.6
Scrophulariaceae	*Scrophularia striata* Boiss.	1	Forb	0.040	11.6
Solanaceae	*Hyoscyamus kurdicus* Bomm. ($n = 5$)	4	Forb	0.19 (0.15–0.24)	139 (112–205)
Zygophyllaceae	*Peganum harmala* L.	*1*, *3*	Forb	0.092	11.6

mine wastes in the UK (6,640 mg/kg; Porter and Peterson 1975), north-eastern Portugal (60–300 mg/kg; de Koe 1994), and a geothermal area in New Zealand (1,766 mg/kg; Robinson et al. 2006). Given the criterion of >1,000 mg/kg foliar As (Ma et al. 2001), such plants could be considered as As hyperaccumulators. However, none of these plants showed the high soil to plant transfer factors typical of hyperaccumulators, suggesting that their high foliar As concentrations may be explained by the combination of extreme tolerance and extreme exposure, rather than distinct physiology. In general, As uptake by plants is largely dependent on the As availability in the soil, as determined by the As source and chemical speciation, pedological factors (pH, Eh, organic matter and colloid contents, soil texture, minerals and drainage conditions), plant species, and plant age (Casado et al. 2007).

In contrast to the findings of Sadiq (1997), and in agreement with our previous study (Karimi et al. 2010), we found the As concentrations in the plants to increase significantly and more or less linearly with the total As concentration in the soil (Fig. 3). The regression slopes for plant As over total soil As in wild plants growing in the Dashkasan and Zarshuran areas revealed that the mean soil-to-plant transfer coefficient was significantly ($p < 0.05$) higher in the Dashkasan area (0.061 versus 0.027). Plotting plant As against water-soluble soil As, instead of total As, yielded a much lower, but still significant correlation coefficient for the Dashkasan area, but a comparable one for the Zarshuran area (Fig. 3). The regression coefficient obtained for plant As over water-soluble soil As was much higher for the Zarshuran area than for the Dashkasan area (181 versus 30; Fig. 3). These data suggest that water-soluble soil As is in fact a poor predictor of As accumulation in plants, particularly when different areas are compared, but also when considering the intra-specific variation within areas, at least within the

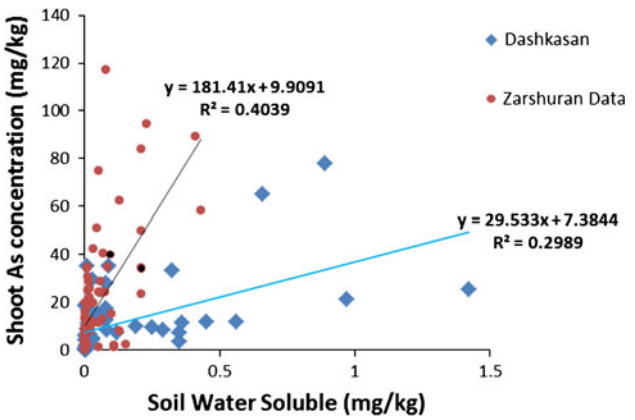

Fig. 3 Shoot As concentrations plotted against soil water soluble As concentrations for samples from contaminated sites of the Dashkasan and Zarshuran deposits in Iran

Dashkasan area. This contradicts the findings of Woolson et al. (1971), and Zandsalimi et al. (2011), who found that water-soluble soil As predicted plant As better than total soil As. The reason for this discrepancy is not clear. It is conceivable that differences between the bulk soil and the rhizosphere might play a role here, particularly in the Zarshuran area.

The arsenic transfer coefficient (AsTC) is defined as the shoot As (mg/kg dry wt) to total soil As (mg/kg dry wt) concentration ratio. It can be used to assess the As accumulation capacity of plants. The AsTC in this study ranged from 0.001 to 0.195 (Table 2), with mean values of 0.045, 0.062, 0.058 and 0.078 at sites 1, 2, 3, and 4, respectively, the differences between sites being insignificant ($p > 0.05$, one-way ANOVA). These values are much lower than those reported by Cao and Ma (2004) for carrot and lettuce (0.1 and 1.6, respectively) growing on CCA-contaminated soils, but higher than those reported by Karimi et al. (2010) for plants growing in the Zarshuran mining area (Fig. 3), and those obtained of Warren et al. (2003) for crops (0.0007–0.032).

The higher mean As transfer coefficient in the Dashkasan area, in comparison with the Zarshuran area, could be due to higher As availability for plant uptake. If so, then the latter is apparently not associated a higher water-soluble fraction, indicating that some part of the soil-bound As must be or become plant available too, at least in the Zarshuran area. The inter-specific variation in AsTC values is considerable in both areas (Fig. 3), and may be attributable to, among other things, variation in rooting depth, mycorrhization, phosphorus demand, root-to-shoot As transfer capacities, or local variations in phosphorus availability (Kabata-Pendias and Pendias 2001). Owing to the chemical similarity of arsenate and phosphate, these two anions compete strongly not only in unspecific anion exchange reactions, but also in specific binding through surface complexation e.g., on iron and aluminium hydroxides surfaces. Moreover, arsenate is thought to be taken up via the phosphate uptake system and may consequently interact with plant P nutrition. Increasing soil phosphate concentrations are therefore expected to cause As–P competition for sorption sites resulting in increased As concentrations in the soil solution, but on the other hand, inhibit As uptake in plant roots via high-affinity P transporters, due to competitive inhibition (Meharg and Macnair 1994).

Mycorrhizal associations and other microbial interactions in the rhizosphere are the most widespread mutualistic symbiotic association between microorganisms and higher plants and can be important for the mineral nutrition of the host plant, in particular the P nutrition (Wilcox 1991). Mycorrhizal fungi may alleviate metal toxicity to the host plant by acting as a barrier for metal uptake (Leyval et al. 1997). Furthermore, numerous bacteria, fungi, yeasts and algae are able to transform As compounds by oxidation, reduction, methylation and demethylation (Frankenberger and Losi 1995). Microbial reduction of As^{V} to As^{III} is known to occur by dissimilatory reduction and detoxification activities of microbes.

Hyperaccumulators initially have been defined as plants that can accumulate $\geq$1,000 mg kg^{-1} of As in shoot dry matter in their natural environment (Baker and Brooks 1989; Ma et al. 2001). Furthermore, in most of the recent publications, additional criteria are being used, usually the combination of an exceptionally high foliar metal concentration, e.g. at least one order of magnitude higher than in 'normal' plants growing at the same sites, a high level of tolerance to the naturally hyperaccumulated metal(s) and a shoot to root metal concentration ratio above or close to unity (Verbruggen et al. 2009). In this study, the highest concentrations of As (113 and 139 mg/kg) were recorded in leaves of *H. oligocephalum* and *H. kurdicus* collected from site 4, which is far below the 1000 mg/kg threshold for As hyperaccumulation. Moreover, the data points for these species are not far above the regression line for plant As over total soil As (Fig. 3). Therefore, none of the species collected from the Dashkasan mining area can be considered a hyperaccumulator of As.

To clean up As-contaminated soils by phytoremediation biotechnology in Iran, it is crucial to select drought-resistant plants with high above ground biomass, short life cycles and high propagation rates that can grow in metal-contaminated and nutrient-deficient soils (Karimi et al. 2009). The soil of the Dashkasan mine area is so heavily contaminated that removal of As using plants grown here is unlikely to be time- and cost-effective. Therefore, the plants grown in these soils can be used to partly remove the bioavailable fraction of As.

An ideal plant for application in phytoextraction should have a high metal tolerance and a high metal accumulation capacity in its harvestable parts (Shi et al. 2009). Most of the terrestrial hyperaccumulators of As identified thus far are pteriod ferns, including the well-known *P. vittata* (Ma et al. 2001; Zhao et al. 2009). The supposed rarity of As hyperaccumulators among terrestrial angiosperms (Karimi et al. 2010) is confirmed by their apparent absence from the Dashkasan area. However, our previous study in the Zarshuran area suggested, for the first time, that terrestrial angiosperm As hyperaccumulators do exist, and that, in particular, *I. cappadocica* Dvorak et Hadac. and *H. persica* Boiss., are two of them. Remarkably, both of these species are robust perennial rosette plants, producing strongly branched inflorescence-bearing stems up to 60 (*I. cappadocica*) or 45 (*H. persica*) cm height in their native habitat. This could make them potential candidates for phytoremediation purposes in Iran. Based on their

relatively high shoot As concentrations and transfer coefficients, it is conceivable that *H. oligocephalum* and *H. kurdicus* could be useful too.

Conclusion

Plants were collected from mining-affected and uncontaminated sites in the Dashkasan area, and the concentration of As in the soils and plants were determined. Total As concentration in the soils ranged from 7 (S1) to 795 (S4) mg/kg As. The As concentrations in plant shoots were generally low with two exceptions, *H. oligocephalum* and *H. kurdicus*, which were able to accumulate up to 113 and 139 mg/kg As in their leaves, while showing relatively high soil-to-plant transfer coefficients, although they cannot be classified as As hyperaccumulators. Comparison of the results obtained from the Dashkasan and the Zarshuran areas confirms the rareness of As hyperaccumulation among terrestrial angiosperms, and suggests that water-soluble soil As does not accurately predict as plant As accumulation.

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References

Adriano DC (2001) Trace Elements in the Terrestrial Environment. Springer, New York

Anawar HM, Garcia-Sanchez A, Murciego A, Buyolo T (2006) Exposure and bioavailability of arsenic in contaminated soils from the La Parrilla mine, Spain. Environ Geol 50:170–179

Asher CJ, Reay PF (1979) Arsenic uptake by barleyseedlings. Aust J Plant Physiol 6:459–466

Ashworth J, Keyes D, Kirk R, Lessard R (2001) Standard procedure in the hydrometer method for particle size analysis. Commun Soil Sci Plant 32:633–642

Baker AJM (1995) Metal hyperaccumulation by plants: our present knowledge of the ecophysiological phenomenon. In: Will plants have a role in bioremediation? 14th Annual symposium on current topics in plant biochemistry, physiology and molecular biology, Columbia, MO, USA, pp 7–8

Baker AJM, Brooks RR (1989) Terrestrial higher plants which hyperaccumulate metallic elements—a review of their distribution, ecology and phytochemistry. Biorecovery 1:81–126

Bohn HL, McNeal BL, O'Connor GA (1985) Soil chemistry. Wiley, New York

Boyle RW, Jonasson IR (1973) The geochemistry of As and its use as an indicator element in geochemical prospecting. J Geochem Explor 2:251–256

Cao X, Ma LQ (2004) Effects of compost and phosphate on plant arsenic accumulation from soils near pressure-treated wood. Environ Pollut 132:435–442

Casado M, Anawar HM, Garcia-Sanchez A (2007) Arsenic bioavailability in polluted mining soils and uptake by tolerant plants (El Cabaco mine, Spain). Bull Environ Contam Toxicol 79:29–35

De Koe T (1994) *Agrostis castellana* and *Agrostis deliculata* on heavy metal and arsenic enriched sites in NE Portugal. Sci Total Environ 145:103–109

Dinkelaker B, Hengeler C, Marschner H (1995) Distribution and function of proteoid roots and other root clusters. Bot Acta 108:183–200

Francesconi K, Visoottiviseth P, Sridokchan W, Goessler W (2002) Arsenic species in an arsenic hyperaccumulating fern, *Pityrogramma calomelanos*: a potential phytoremediator of arsenic-contaminated soils. Sci Total Environ 284:27–35

Frankenberger WT Jr, Losi ME (1995) Applications of bioremediation in the cleanup of heavy metals and metalloids. In: Skipper HD, Turco RF (eds) Bioremediation: science and applications. Soil Science Society of America Special Publication No. 43, Madison, pp 173−210

Gulz PA, Gupta SK, Schulin R (2005) Arsenic accumulation of common plants from contaminated soils. Plant Soil 272:337–347

Jiang QQ, Singh BR (1994) Effect of different forms and sources of arsenic on crop yield and arsenic concentration. Water Air Soil Pollut 74:321–343

Kabata-Pendias A, Pendias H (2001) Trace elements in soils and plants, 3rd edn. CRC Press LLC, Boca Raton

Karimi N, Ghaderian SM, Raab A, Feldman J, Meharg AA (2009) An arsenic accumulating, hypertolerant brassica, *Isatis cappadocica*. New Phytol 184:41–47

Karimi N, Ghaderian SM, Maroofi H, Schat H (2010) Analysis of arsenic in soil and vegetation of a contaminated area in Zarshuran, Iran. Int J Phytoremediat 12:159–173

Kavanagh PJ, Farago ME, Thornton I, Braman RS (1997) Bioavailabilty of arsenic in soil and mine wastes of the Tamar valley, SW England. Chem Spec Bioavailab 93:77–81

Khattak AK, Page AL, Parker DR, Bakhtar D (1991) Accumulation and interactions of arsenic, selenium, molybdenum and phosphorus in Alfalfa. J Environ Qual 20:165–168

Kirk GJD, Santos EE, Findenegg GR (1999) Phosphate solubilisation by organic anion excretion from rice (*Oryza sativa* L.) growing in aerobic soil. Plant Soil 211:11–18

Koch I, Wang L, Reimer KJ, Cullen W (2000) Arsenic species in terrestrial fungi and lichen from Yellowknife, NWT, Canada. Appl Organomet Chem 14:245–252

Lescuyer JL, Hushmand ZA, Daliran F (2003) Gold metallogeny in Iran: a preliminary review. In: Eliopoulos DG et al (eds) Mineral exploration and sustainable development, vol 2. Millpress, Rotterdam, pp 1185–1188

Leyval C, Turnau K, Haselwandter K (1997) Effect of heavy metal pollution on mycorrhizal colonization and function: physiolgical, ecological and applied aspects. Mycorrhiza 7:139–153

Lombi E, Sletten RS, Wenzel WW (2000) Sequentially extracted arsenic from different size fractions of contaminated soil. Water Air Soil Pollut 124:319–332

Ma LQ, Komar KM, Tu C, Zhang W, Cai Y, Kennelley ED (2001) A fern that hyperaccumulates arsenic. Nature (London) 409:579

Marin AR, Masschenlyn PH, Patrick WH (1993) Soil redox-pH stability of arsenic species and its influence on arsenic uptake by rice. Plant Soil 152:245–253

Matschullat J, Perobelli-Borba R, Deschamps E, Figueiredo BR, Gabrio T, Schwenk M (2000) Human and environmental contamination in the Iron Quadrangle, Brazil. Appl Geochem 15:181–190

McGrath SP, Sidoli CMD, Baker AJM, Reeves RD (1993) The potential for the use of metal-accumulating plants for the in situ decontamination of metal polluted soils. In: Eijasackers HJP, Hamers T (eds) Integrated soil and sediment research: a basis for proper protection. Kluwer Academic Publishers, Dordrecht, pp 673–676

Meharg AA, Jardine L (2003) Arsenite transport into paddy rice (*Oryza sativa*) roots. New Phytol 157:39–44

Meharg AA, Macnair MR (1994) Relationship between plant phosphorus status and the kinetics of arsenate influx in clones of *Deschampsia caespitosa* (L.) Beauv. that differ in their tolerance of arsenate. Plant Soil 162:99–106

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

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 origen. Econ Geol 101:1–25

Neumann G, Römheld V (1999) Root excretion of carboxylic acids and protons in phosphorous-deficient plants. Plant Soil 211: 121–130

Pongratz R (1998) Arsenic speciation in environmental samples of contaminated soil. Sci Total Environ 224:1–3

Porter EK, Peterson PJ (1975) Arsenic accumulation by plants on mine wastes (United Kingdom). Sci Total Environ 4:365–371

Pratas J, Prasad MNV, Freitas H, Conde L (2005) Plants growing in abandoned mines of Portugal are useful for biogeochemical exploration of arsenic, antimony, tungsten and mine reclamation. J Geochem Explor 85:99–107

Rafiei B, Bakhtiarinejad M, Hashemi M, Khodaei AS (2010) Distribution of heavy metals around the Dashkasan Au mine. Int J Environ Res 4:647–654

Rastad E, Niroumand SA, Emami MH, Rashidnejad ON (2002). Genesis of Sb–As–Au deposit in Dashkasan volcano-plutonic complex (east Qorveh, Kordestan province). Iran Geosci J 37–38:2–23

Reza R, Singh G (2010) Heavy metal contamination and its indexing approach for river water. Int J Environ Sci Technol 7(4):785–792

Robinson B, Duwig C, Bolan N, Marchetti M, Moni C, Schroeter L, Dijssel C, Milne G, Clothier B (2006) Arsenic hyperaccumulation by aquatic macrophytes in the Taupo Volcanic Zone, New Zealand. Environ Explor Bot 58:206–215

Sadiq M (1997) Arsenic chemistry in soils: an overview of thermodynamic predictions and field observations. Water Air Soil Pollut 93:117–136

Sheppard SC (1992) Summary of phytotoxic levels of soil arsenic. Water Air Soil Pollut 64:539–550

Shi WY, Shao HB, Li H, Shao M, Du S (2009) Progress in the remediation of hazardous heavy metal-polluted soils by natural zeolite. J Hazard Material 170:1–6

Smith E, Naidu R, Alston AM (2002) Chemistry of inorganic arsenic in soils: II. Effect of phosphorus, sodium, and calcium on arsenic sorption. J Environ Qual 31:557–563

Soon YK, Abboud S (1991) A comparison of some methods for soil organic carbon determination. Commun Soil Sci Plant Anal 22:943–954

Verbruggen N, Hermans C, Schat H (2009) Mechanisms to cope with arsenic or cadmium excess in plants. Curr Opin Biol 12:1–9

Warren GP, Alloway BJ, Lepp NW, Singh B, Bochereau FJM, Penny C (2003) Field trials to assess the uptake of arsenic by vegetables from contaminated soils and soil remediation with iron oxides. Sci Total Environ 311:19–33

Welch RM (2002) Micronutrition of plants. Crit Rev Plant Sci 14:49–82

Wenzel WW, Adriano DC, Salt D, Smith R (1999) Phytoremediation: a plant–microbe-based remediation system. In: Adriano DC, Bollag JM, Frankenberger WT Jr, Sims RC (eds) Agronomy monograph, vol 37. Madison, USA, pp 456–508

Wilcox HE (1991) Mycorrhiza. In: Waisel Y, Eshel A, Kafkafi U (eds) Plant roots, the hidden half. MarcelDekker, New York, pp 731–765

Wong MH (2003) Ecological restoration of mine degraded soils with emphasis on metal contaminated soils. Chemosphere 50: 775–780

Woolson EA, Axley JH, Kearney PC (1971) Correlation between available soil arsenic, estimated by six methods, and response of corn (*Zea mays* L.). Soil Sci Soc Am Proc 35:101–105

Xu J, Thornton I (1985) Arsenic in garden soils and vegetable crops in Cornwall: implications for human health. Environ Geochem Health 7:131–133

Zandsalimi S, Karimi N, Kohandel A (2011) Arsenic in soil, vegetation and water of a contaminated region. Int J Environ Sci Technol 8(2):331–338

Zhang W, Cai Y, Tu C, Ma LQ (2002) Arsenic speciation and distribution in an arsenic hyperaccumulating plant. Sci Total Environ 300:167–177

Zhao FJ, Ma JF, Meharg AA, McGrath SP (2009) Arsenic uptake and metabolism in plants. New Phytol 181:777–794