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Speciation and Phytoavailability of Heavy Metals in Contaminated Soils in Sarcheshmeh Area, Kerman Province, Iran

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Abstract Heavy metal content in soil and the most abundant indigenous plant species (*Artemisia sieberi*) in Sarcheshmeh area is investigated. Sequential extraction analysis is carried out and phytoavailable fractions of selected heavy metals are also determined. The results show that heavy metals in the study area are potentially bioavailable. Calculated transfer factor (mean value for Cu: 5.7; As: 8.9; Pb: 4.1; Mo: 7.2; Cd: 1.9; and Zn: 1.8) and heavy metal concentration in plant species indicate that metal contamination is already transferred to *Artemisia sieberi* which proved to behave like an accumulator plant and hence poses a serious threat to local population. Contamination is mostly the result of three decades of ore smelting at the Sarcheshmeh copper complex.

Keywords Pollution · Phytoavailability · Sequential extraction · Sarcheshmeh

Soil is a key element in all terrestic ecosystems. It provides the nutrient bearing environment for plant life and is of essential importance for degradation and transfer of biomass (Bradl 2004). Contamination of soil with potentially toxic metals (PTMs) poses serious risks for biota and human health. At low concentrations, some PTMs (e.g. Cu, Cr, Mo, Se and Zn) are essential to healthy functioning and reproduction of microorganisms, plants and animals (Alloway 1995). However, at high concentrations, these essential elements may cause direct toxicity or reproduction effects. Risk management based only on the total or "pseudototal" content of PTMs in soil might minimize the risks, assuming that pollutants transferring to water resources or biota increase with contamination level. However, total analysis gives no idea of the extent to which elements are really transferable or bioavailable. Soil–plant transfer of PTMs is a part of chemical element cycling (Adamo and Zampella 2008).

Regions where mining and smelting have been in operation for a long time are potential candidates for a wide range of pollutant elements into the environment. In the vicinity of nonferrous metal smelters, high concentrations of toxic compounds have been detected in soils and vegetations (e.g. Ettler et al. 2005). The main sources of trace elements for plants are their growth media from which trace elements are taken up by the roots or by the foliage (Fytianos et al. 2001). Although soil total concentration of metals is commonly used in establishing environmental quality standards, its usefulness to predict soil-to-plant transfer is often questioned, since the speciation and bioavailability of the metals in soils vary greatly depending upon soil physico-chemical properties (Wang et al. 2006).

The main objective of this paper is to study the impact of polluted soil (by copper smelting) on the most abundant indigenous plant species (*Artemisia sieberi*) in the vicinity of Sarcheshmeh copper complex (Kerman province, central Iran) and also to investigate the transfer of selected toxic metals (As, Cu, Mo, Zn, Cd, and Pb) through examining their phytoavailability and speciation.

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Materials and Methods

Fifty seven samples (19 topsoil (0–5 cm), and 38 plant (*Artemisia sieberi)* samples were collected in the vicinity of the smelter. Each composite soil sample comprised five subsamples. The sampling sites were chosen close to the population centers both in the upwind and downwind directions. Rastmanesh et al. (2010) control point is taken as local geochemical baseline.

Plant samples (leaves and roots) were also collected at each sampling site. Plant sampling was composite and each sample consisted of at least 10 bushes. The samples were then divided into leaves and roots. Apart from being the dominant plant species in the area, *Artemisia sieberi* is also used as an herbal medicine and livestock forage by the local population.

In the laboratory, soil samples were air dried at room temperature, sieved through a 2-mm steel-wire sieve and were ground in an agate mill.

Plant samples were first washed with tap water, followed by de-ionized water. Washing was carried out rapidly to avoid possible loss of adsorbed ions. All analyses were carried out at ACME laboratories Ltd. (ISO 9001:2000) in Canada. Replicate samples (about 5% of samples) were also analyzed to test precision. In these analyses concentrations of As, Cu, Mo, Pb, Zn and Cd were measured.

In order to determine the phytoavailability of elements in soil samples, the procedure suggested by Jamali et al. (2006) was used.

The soil to plant transfer factor (TF) (also known as uptake factor, accumulation factor, concentration factor), is an index for evaluating the transfer potential of a metal from soil to plant. The transfer factor is generally defined as the ratio of metal concentration in plant to the total metal concentration in soil (Wang et al. 2006).

In this study transfer factor (TF) was calculated as heavy metal content in plant (root and leave) divided by phytoavailable concentration in soil. Eight soil samples were selected for sequential extraction analysis. Description of these samples is given in Table 2. The stations were selected in such a way to investigate variation in heavy metal speciation with depth and distance to the smelter. The procedure of Tessier et al. (1979) was used to partition heavy metals into five fractions (i.e. exchangeable fraction (F1), bound to carbonate (F2), bound to Fe/Mn oxides (F3), bound to organic matter (F4) and the residual phase (F5)). The extraction was carried out progressively on initial one gram aliquots of dry soil samples. All extracted solutions were analyzed for the selected heavy metals using ICP-OES (Model: Genesis, Spectro). The accuracy of the measurements was checked using SPEX Certi Prep standards (ISO:9001) and Merck standard solutions. The precision of the measurements was checked triplicate measurements of target elements in each extract. The mean concentrations are reported. To assess the accuracy and reproducibility of the sequential extraction results in the soil samples, the recovery percents were also calculated as follows:

$$R = \frac{(C_{F1} + C_{F2} + C_{F3} + C_{F4} + C_{F5})}{C_{total}} \times 100$$

Percent recovery ranges from 86% to 130% indicating good agreement between total values and sum of fractions (e.g. Burt et al. 2003).

Results and Discussion

Table 1 shows maximum, minimum and mean concentrations of measured elements in soil samples together with metal concentration in control point. According to Table 1, it is clear that Sarcheshmeh soil is enriched in all measured elements especially Cu relative to the control point. The polluting role of Sarcheshmeh smelter is already discussed by Rastmanesh et al. (2010).

According to Kabata-Pendias and Pendias (2001), several reports have already indicated that regardless of the forms of the anthropogenic trace metals, their availability to plants is significantly higher than those from natural origin. Table 1 also shows minimum, maximum and the mean concentration of phytoavailable components of the analyzed soil samples. In general, phytoavailable content of heavy metals is much higher in the most contaminated sites and is considerable for all stations.

The phytoavailable metals are highly correlated. Moreover negative correlation between phytoavailable content of metals and distance from the smelter indicates decreasing phytoavailability with increasing distance. There is also significant positive correlation between total metal contents in soil and their phytoavailable contents. Thus, it may be concluded that anthropogenic inputs from the smelter are the main contributors of phytoavailable metals in soil samples.

According to Ma and Rao (1997) assuming that bioavailability is related to solubility, metal bioavailability decreases in the order:

Table 1 Max. Min. and mean of measured elements in soils together with their mean phytoavailable content (all values are in mg/kg)

	DL	Min	Max	Mean	Phytoavailable content (mean)	Control site
Cu	0.01	64	11500	1212.7	255.3	78
As	0.1	28.5	420	114	14.2	30.5
Pb	0.01	8	315	65	46.5	10
Mo	0.01	0.8	55	6.5	1.3	0.9
Cd	0.01	0.2	11.5	2	0.3	0.3
Zn	0.1	69	486	161.1	70.6	69

DL detection limit

Table 2 Mobility factor for measured heavy metals (in percent)

Sample	Distance and direction to the smelter	Cd	Mo	Cu	As	Zn	Pb
S1	12.5 km, NW	18.5	9.1	2.8	7.5	4.9	2.6
S2	1.5 km, W	84	23.5	23.7	21.6	16	25
S3	1 km, W	59.7	19	17.3	9.3	16.8	32.9
S4	500 m, N	63.7	12.8	23.4	35	17	54.5
S5[a]	500 m, N	44	15.1	22.9	22.1	5.1	11.7
S6[b]	500 m, N	16.7	12.1	17.2	13.6	6.2	3.2
S15	8 km, N	87.6	16.4	21.5	20.5	2.9	21.8
S18	5 km, N	81.8	19.2	22.7	34	13.6	34

[a] Subsoil sample of S4

[b] Deep sample of S4

$$\text{Exchangeable} > \text{carbonate} > \text{Fe} - \text{Mn oxide} > \text{organic} > \text{residual}$$

Thus metals in the non-residual fractions are more bioavailable than in residual fraction. It can be said that non-residual fractions are higher in Cd, Cu and As. In the case of Zn and Mo, residual and non-residual fractions are nearly equal. The average percent of non-residual fractions for the measured metals is as follows: Cu: 75.8; Cd: 81.6; and for As: 73; These values are 58.5 for Pb; 52.6 for Zn; and 49.5 for Mo. These results indicate that heavy metals in Sarcheshmeh soils are potentially bioavailable.

Evaluating heavy metal speciation in selected stations reveals that non-residual fractions are considerably higher in surface soils and also in stations close to the smelter.

For the measured heavy metals fractionation is as follows:

$$\text{Cu}: F4 > F3 > F5 > F2 > F1$$
$$\text{Zn}: F5 > F3 > F2 > F4 > F1$$

$$\text{Cd}: F2 > F5 > F4 > F3 > F1$$
$$\text{As}: F3 > F5 > F1 > F2 > F4$$

$$\text{Mo}: F5 > F3 > F1 > F4 > F2$$
$$\text{Pb}: F5 > F2 > F3 > F4 > F1$$

The results are similar to previous studies (e.g. Kabala and Singh 2001; Hu et al. 2006). Residual fraction constitutes a significant proportion for all elements. This is especially true for Mo, Zn and Pb. According to Kaasalainen and Yli-Halla (2003) the proportion of the residual fraction reflects native metal concentration in soil. Considering that, Sarcheshmeh area is a metallogenic province; contribution of native metals in enriching the surface horizons in the investigated heavy metals is not unreasonable.

The mobility of heavy metals in soil samples can be evaluated through dividing the fractions weakly bound to soil components by all fractions (Kabala and Singh 2001) as follows:

$$\text{MF} = \frac{(F1 + F2)}{(F1 + F2 + F3 + F4 + F5)} \times 100$$

The results are shown in Table 2. According to Table 2, the lowest MFs are related to those stations located farther from the smelter and also in deep soils. Higher MF values for other stations are a potential risk for transferring toxic metals to plants. Among the measured elements, the highest MF belongs to Cd, reflecting the potential high risk of this toxic and non-essential element to the health of living organisms. Considering oxidizing conditions of the surface environment and the soil pH values (5.5–7.5), it is reasonbale to assume that Cu accurse as metallic Cu, while Pb and Cd occur as Pb^{2+} and Cd^{2+}, respectively. Arsenic is probably presents as $HAsO^{4-}$ or H_2AsO^4.

Analyzed elements Concentrations in *Artemisia sieberi* are presented in Table 3. The sufficient and toxic heavy metal content in leaves (Kabata-Pendias and Pendias 2001) are also presented. Elemental concentrations indicate that this species acts as an accumulator plant (Siegel 2002) especially for Cu. Cadmium content is also alarming in most of the sampled stations. Pb concentration in leaves is more than sufficient level. Comparison of elemental content in leaves with toxic levels, indicates that Cu and As concentration exceeds toxic levels. Furthermore, concentrations of Cd, Pb and Zn are within the toxic range in the more polluted stations.

Negative correlation between heavy metal content and distance from the smelter in plants indicates decreasing elemental concentrations with increasing distance. Also

Table 3 Heavy metal contents in *Artemisia sieberi* together with sufficient and toxic levels in leaves (Kabata-Pendias and Pendias 2001) (all values are in mg/kg)

	Leaves			Root + leave	Sufficient level	Toxic level
	Min	Max	Mean	Mean		
Cu	33	3310	321.3	558.7	5–30	20–10
As	5.7	108	22.6	35.5	1–1.7	5–20
Pb	2.5	87	20.8	37	5–10	30–300
Mo	0.8	10	3.1	4.9	0.2–5	10–50
Cd	0.2	7.8	1.4	2.4	0.05–0.2	5–30
Zn	36	185	66	101.6	27–150	100–400

negative correlation between soil pH and elemental content in plant samples reveals decreasing elemental uptake with increasing pH. Low positive correlation between metal content in plants and organic matter in soil also reflects the minor role of organically-bound metals as an elemental source. Sequential extraction analysis results indicate that this is especially true for Cu.

Calculated TF values are considerable for all elements (mean TF value for Cu: 5.7; As: 8.9; Pb: 4.1; Mo: 7.2; Cd: 1.9; and Zn: 1.8). According to Alloway (2005) TF values between 1 and 10, reflect intensive accumulation of heavy metals.

Higher TF either reflects relatively poor retention in soils, or greater efficiency of plants to absorb metals (Yan et al. 2007). Significant TF values for all elements reflect the ease of uptake of metals by sampled plants. This is in agreement with the relatively high phytoavailable measured heavy metals in soil samples. However, elemental uptake through leaves should not be overlooked. Seemingly, high TF values for *Artemisia sieberi* reflect the accumulating nature of this species. Significant TF values for non-essential elements such as As, and Pb, poses a potential risk to animal and human health.

Mean concentration of trace elements in leaves of *Artemisia sieberi* are higher than those of roots indicating that elements are easily transferred to leaves. The ease of translocation of heavy metal from roots to leaves and uptake of heavy metals through leaves are other reasons for the observed high metal contents in leaves.

In conclusion it can be said that copper smelting in Sarcheshmeh copper complex has resulted in soil pollution. Comparison of heavy metals concentrations in sampling sites with those in control site show considerable enrichment of heavy metals in soil.

Sequential extraction analysis showed relatively limited metal mobilities especially in the case of deep soils and distant stations from the smelter, probably indicating geogenic contribution.

Concentration of metals in *Artemisia sieberi* is significant. Considerable phytoavailable content of heavy metals in soil, the sandy texture and relatively low organic matter content of the soils (Rastmanesh 2009) may play a significant role in higher mobility of metals to plants. Considerable TF values may indicate great efficiency of *Artemisia sieberi* in metal uptake. Elemental uptake from leaves and deeper soil may provide significant sources of heavy metals to plants.

Since *Artemisia sieberi* is mostly used as forage for livestock grazing, it may provide a pathway for heavy metals to enter the food chain and hence pose a potential threat to the health of human.

Finally it must be noted that continuous copper smelting can result in acidic conditions in soil. This in turn will facilitate the transfer of toxic elements such as Cd to plants. Also dry deposition on leaves should not be ignored; since the leaves are eaten by herbivores unwashed. Analyzed deposited particulates on leaves (Rastmanesh 2009) indicated high concentration of heavy metals. Livestock grazing should be restricted in adjacent areas to the smelter. Medical geology investigations must also be carried out to assess probable accumulation of heavy metals in livestock and humans.

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