

Heavy metal concentration and speciation in Sarcheshmeh soil, Kerman Province

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Abstract

Copper smelting in Sarcheshmeh copper complex poses a serious threat to soil contamination by toxic heavy metals (As, Cu, Mo, Cd, Pb, Zn). In this study assessment of induced pollution to soil is carried out and heavy metal speciation is investigated. Calculated geoaccumulation index (I_{geo}) indicate that the most polluted stations are those close to the smelter and also in the prevailing wind directions. Also the level of contamination is rapidly decreased with increasing distance from the smelter. This is in agreement with statistical results which also confirm decreasing elemental concentration with increasing distance from the smelter. Sequential extraction analyses indicate that metal mobility is not significant and the exchangeable fraction is negligible in most cases. The results of mobility factor calculation reflect decreasing heavy metal mobility with depth and also distance from the smelter. Furthermore, residual fraction constitutes a major fraction especially in the case of Pb, Mo and Zn. This may reflect contribution of native elements in topsoil enrichment, especially in areas distant from the smelter.

Keywords: Heavy metal, Soil pollution, Speciation, Mobility, Geoaccumulation index

1. Introduction

Soil plays a vital role in human life as the very survival of mankind is tied to the preservation of soil productivity (Kabata-Pendies and Mukherjee, 2007). According to Chen et al. (1997) soil is apart from being a medium for plants to grow is also a transmitter of many pollutants including potentially toxic metals into the atmosphere, biosphere and water resources. A major contaminant source soil, especially when it comes to the dry deposition of heavy metals, is smelting of ore minerals. Managing contaminated soil in different environments requires an understanding of heavy metals concentrations, the scale of contamination and the source of the heavy metals in that particular environment (Luo et al., 2007). 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. 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 Sarcheshmeh porphyry copper mine is located in the central Iranian volcanic belt, in Kerman province of Iran (fig.1). The deposit contains 1200 million tons of ore of 0.69% Cu and 0.03 Mo (Shahabpour and Doorandish, 2008).

The porphyry copper mineralization at Sarcheshmeh is associated with a granodioritic stock intruded into a folded and faulted early Tertiary volcano-sedimentary rocks, (mainly andesite

porphyries) Waterman and Hamilton, 1975). Wall-rock alteration pattern in Sarcheshmeh is comparable to other porphyry Cu deposits worldwide with some local peculiarities and is basically composed of potassic, argillic, and propylitic zones with a overprinted phyllic alteration. Sarcheshmeh copper complex consists of a large open pit mine along with mineral dressing, smelting and molding plants.

The main objectives of this study are to assess the soil pollution using geoaccumulation index (Muller, 1969), investigating the role of copper smelting in the Sarcheshmeh area, and to determine heavy metal mobility in the soil samples.

2. Materials and methods

A total of 32 topsoil samples (0-5cm) were collected from 32 sampling stations in Sarcheshmeh area (Fig.1). Most stations are located in the prevailing wind directions i.e. S-N and SW-NE. In order to determine the local geochemical baseline a control point (S5) was also chosen and sampled 12.5 km west of the smelting plant (fig.1). Approximately 1kg of composite soil sample was collected in each station using a stainless steel spade. Each composite sample consisted of 5 randomly collected subsamples from a 10m² area. The subsamples were thoroughly mixed to obtain a composite sample. The geographical coordinates of each sampling station was recorded by GPS and plotted in figure 1. The coarse hard rock fragments and plant litter was removed and the soil samples were allowed to dry at room temperature for 3 days. The dried samples were sieved and less than 2 mm fraction was separated. A part of this fraction was ground and sent to AMDEL laboratories (Amdel limited labs ISO 9001) in Australia for analysis. Six soil samples from 6 stations (S4, S5, S9, S10, S15, and S18) were selected for sequential extraction analysis. 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. The extraction was carried out progressively on initial one gram dry soil sample. The extracted fractions are as follows: Exchangeable fraction (F1); Bound to carbonate (F2); Bound to Fe/Mn oxides (F3); Bound to organic matter (F4); Residual phase (F5).

3. Results and discussion

Concentrations of the measured elements in topsoils are summarized in table 1. Elemental concentrations in the control point are given for comparison. When compared with the control point, heavy metals are enriched in topsoil samples, with the highest enrichment in stations close to the smelter probably resulting wet and dry deposition of heavy metal-polluted dusts. This is also well reflected in high significant correlation coefficients between the measured trace elements (table 2), and the negative correlation between elements and the distance from the smelter.

The geoaccumulation index includes seven classes in which zero and smaller values fall within the uncontaminated class and those greater than 5 falls into the very seriously polluted class (e.g. Hu et al., 2006). In this study, I_{geo} was calculated using metal concentrations in control site. Details of the I_{geo} values for individual elements are presented in figure 2.

Considering figure 2 and the contamination levels, topsoils adjacent to the smelter are very seriously polluted with potentially toxic metals such as Cu, Cd, Sb, Pb and Mo. The lowest contamination degree belongs to Zn. Spatial variation of I_{geo} (not shown here) obviously

reveals that the most contaminated stations are those close to the smelter. Reduced contamination with distance from the smelter and also in upwind direction.

may indicate that particulate size metals can be an important factor for induced soil pollution. For instance, soil contamination with Zn, is very high adjacent to the smelter, while the rest of the stations are uncontaminated. For some elements such as Cu and Cd, most of the stations are contaminated to varying degrees, with the highest contamination occurring in the stations adjacent to the smelter. This may indicate that Cu is carried by a broad range of particulate size, and hence distributed widely. However further investigation is needed to confirm this assumption.

According to the Muller scale "uncontaminated" pollution of various metals for most upwind stations is indicated. This reflects the fact that soil pollution is mostly restricted to a few kilometers from the smelter.

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

Exchangeable> carbonate> Fe-Mn oxide> organic> residual

Thus metals in the non-residual fractions are more bioavailable than in residual fraction (Olajire et al. 2003). The results of sequential extraction are shown in figure 3. 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. Evaluating heavy metal speciation in selected stations reveals that non-residual fractions are considerably more for stations close to the smelter. The exchangeable fraction is only significant for As (Av: 19.1%) and Mo (Av: 16.3%). Carbonate fraction is an important fraction for Cd (mean: 62.3%) and somehow for Pb (mean: 26.8%). Fe-Mn oxide fraction constitutes a considerable proportion especially in the case of As, Zn, Pb and Cu. High proportion of trace metal association with oxide phases is indicative of anthropogenic pollution (Farkas et al. 2007). Organic matter fraction is significant only for Cu (AV: 30%). High affinity of Cu to organic matter is frequently reported (e.g. Hu et al. 2006). Residual fraction constitutes a significant proportion for all elements. According to Kaasalainen and Yli-Hilla (2003) the proportion of the residual fraction reflects native metal concentration in soil.

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:

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

The results are shown in table 3. According to table 3, the lowest MFs are related to control point (S5). Higher MF values for other stations are a potential risk for transferring toxic metals to plants. Among the measured elements, the highest MF is belongs to Cd, reflecting the potential high risk of this toxic and non-essential element to the health of living organisms. Table 3, indicates that MF values decreases with distance from the smelter.

4. Conclusions

Topsoil in the vicinity of Sarcheshmeh copper complex is highly enriched in potentially toxic metals. The results of statistical analysis indicate strong trace element associations. Decreasing soil pollution with increasing distance from the smelter reflects the major role played by ore smelting in soil pollution. Sequential extraction analysis show relatively

limited metal mobility especially far from the smelter. This may indicate contribution of geogenic metals in soil enrichment.

Although, the results of this study show that smelter plays a major role in polluting the soil, the role played by parent material and biogeochemical processes (Reimann and Caritat, 2005), in topsoil enrichment should not be overlooked.

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Table 1: elemental concentration in topsoil samples (in ppm)

	Min	Max	Mean	Median	Control point
As	22	531	124.1	65.8	30.5
Cu	64	12100	1589.2	390	78
Pb	9	403	90.3	49	10
Zn	69	894	210	130.5	69
Mo	0.8	94.5	10.4	3.4	0.9
Cd	0.2	12.8	2.9	1.6	0.3
Sb	0.4	50.5	6.2	3.2	0.4

Table 2: Pearson's correlation coefficient of topsoil data

	As	Cu	Mo	Zn	Sb	Cd	Pb	Al	Fe	Mn	Dist.
As	1										
Cu	.572	1									
Mo	.646	.894	1								
Zn	.611	.831	.856	1							
Sb	.606	.931	.944	.826	1						
Cd	.570	.944	.910	.895	.920	1					
Pb	.575	.858	.840	.897	.824	.927	1				
Al	-.153	-.228	-.272	.000	-.366	-.140	-.006	1			
Fe	<u>.397</u>	.186	.195	.370	.143	.204	.216	<u>.487</u>	1		
Mn	.223	.215	.213	<u>.471</u>	.095	.252	.347	.626	.632	1	
Dist.	-.646	-.840	-.863	-.725	-.896	-.819	-.744	.332	-.107	-.112	1

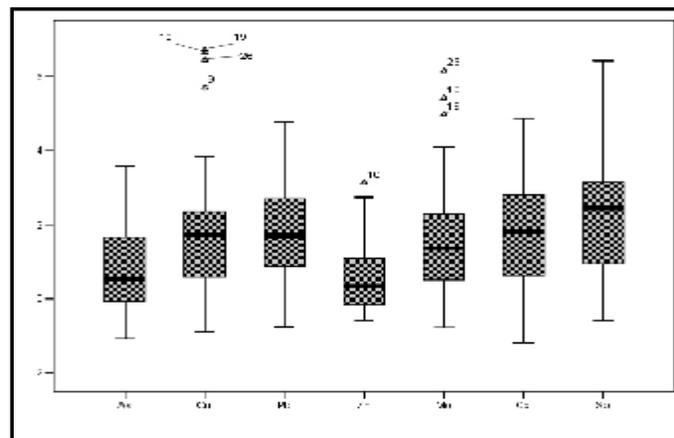
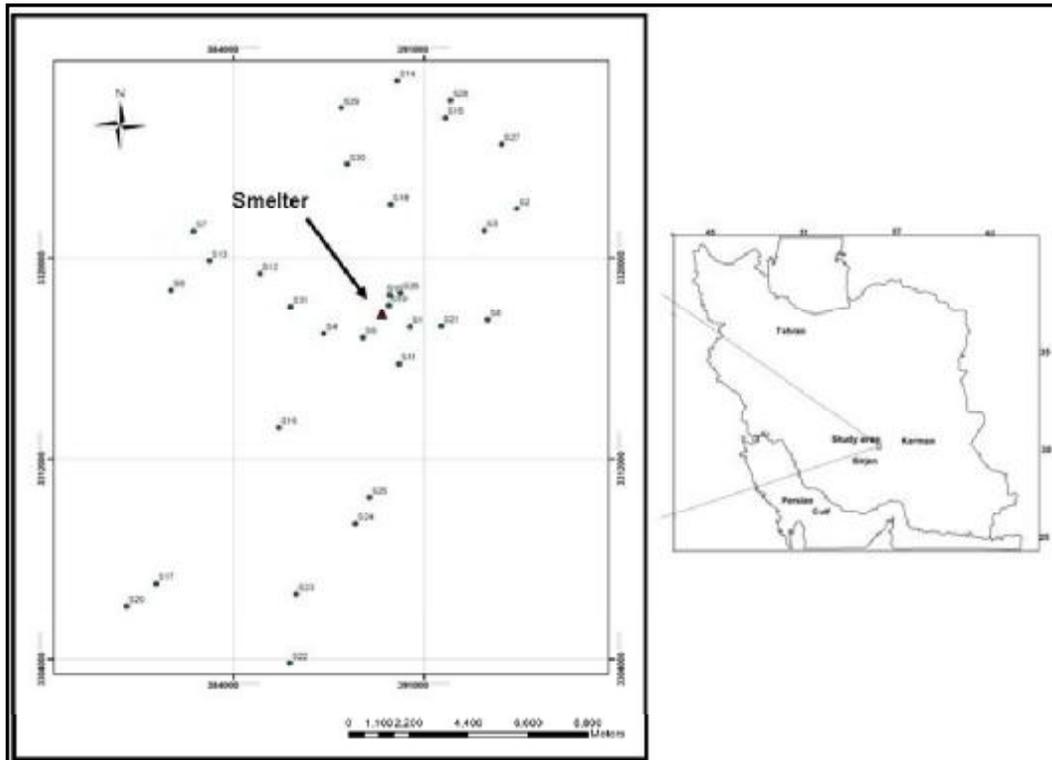
Correlation is significant at the 0.01 level (2-tailed).

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

Dist: Distance from the smelter

Table3: Results of MF calculation (in percent)

	Cu	As	Zn	Pb	Cd	Mo
S5	2.8	7.5	4.9	2.6	18.5	9.1
S4	23.7	21.6	16	25	84	23.5
S9	17.3	28.6	16.8	35	59.7	19
S10T	23.4	35	17	54.5	63.7	12.8
S15	21.5	2.5	2.9	21.8	87.6	16.4
S18	22.7	34	13.6	34	81.8	19.2



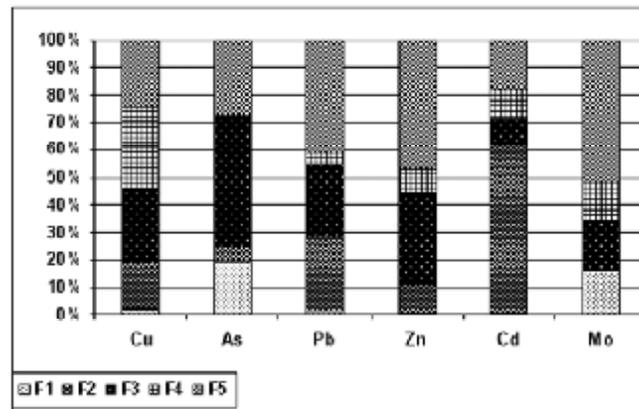


Figure 3: elemental fractionation in soil samples