

Trace element concentration and bioavailability in soils and plants in the vicinity of Miduk Copper mine, Kerman, Iran

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Abstract

*The accurate estimation of metal bioavailability in soils is becoming more important in ecological risk assessment. In this study, 60 soil samples at two depths (0-5cm and 15-20 cm) in the vicinity of Miduk Porphyry Copper Mine, Kerman Province, Iran, were analyzed for total concentration of 45 elements. To determine the bioavailability of various heavy metal forms, sequential extraction analysis was carried out. Average concentration of Ag, As, Cd, Cu, Ni and Pb soil samples are 0.88, 28.57, 0.6, 482.69, 53.05 and 122.3 mgkg⁻¹, respectively. In order to assess the possible bioaccumulation of these elements, the roots and the overground parts of 3 plant species (*Astragalus-Fabaceae*, *Acanthophyllum -Caryophyllaceae*, *Artemisia -Asteraceae*) were collected and analysed. The concentration of elements in the root and the overground parts of the plants are compared with geochemical distribution of the analysed elements in soil. As expected, it has been observed that topsoil samples (0-5cm) have higher levels of Ag, Cr, Cu, Fe, Mo, Se and Pb than subsoil samples (15-20cm). The highest transfer factor (T_f) in these three plant species is found for Cd, Mo, Cu, and the lowest is for Cr, Co and Al. High levels of As, Cu and Ag in soil samples poses a potential risk in the area.*

Keywords: *Miduk porphyry copper mine; Iran; trace element; topsoil; subsoil; bioavailability; sequential extraction.*

1. Introduction

Mining can be a significant source of metal contamination in the environment owing to activities such as mineral excavation, ore transportation, smelting and refining, disposal of tailings, and waste water around mines (Chopin and Alloway, 2007; Chen et al. 2007) furthermore, mining and smelting are considered to be two of the main sources of Cu, Pb and Zn pollution in the environment (Alloway and Ayres, 1997). High level metals are usually found in superficial soil and vegetation in areas affected by mining activities (Liu et al, 2006) however, different distributions of elements in chemical fractions, which have different bioavailability (Maiz et al, 2000) cause a poor relationship between plant uptake and total content of elements in soil (Wang et al, 2003). Total trace metal analysis may provide information concerning possible concentration of metals in soil, but generally this is not a sufficient criteria to estimate the environmental implications of their presence because availability and uptake of trace elements by organisms depends more on their speciation than on the total content (Gue et al, 2006).

Sequential extraction scheme is one of the most widely used techniques to estimate metal mobility in soils. This technique gives information on the element distribution among different phases of soil and helps to predict the potential effects of metal contamination in soils. Among different fractions, only soluble and exchangeable metal species in the soils are the available fractions for plant uptake (Chen et al, 2007). Residual fraction is considered immobile and tightly bound and may not be expected to be release under natural conditions. The main objectives of this study are: (1) to describe the distribution pattern of elements in soils of Miduk area. (2) to assess the fractionation of elements in soil and (3) investigate the uptake of each element by the plants considering its concentration in plant species.

2. Material and Methods

The Miduk porphyry Cu deposit (55° 10' E, 30° 25' N) is located in the Dehaj–Sarduiyeh district, on La Chah Mountain about 45 km northeast of Shahr-e-Babak as a part of the Urumiyeh-Dokhtar magmatic belt (Fig 1). Intensive (open pit) mining has been active at Miduk deposit since 1996. The lowest and highest annual average temperature are -15 and 35 °C, respectively and the average annual rainfall is 256 mm. 30 soil samples from different locations in the study area were collected in May 2009 (Fig1). At each site, surface (0-5cm) and subsurface (15-20cm) soils were sampled. Also, three plant species: *Astragalus* (Fabaceae), *Acanthophyllum* (Caryophyllacea) and *Artemisia* (Asteraceae) were collected from the same stations where soil samples were collected. Soil samples were dried for 7 days at room temperature and then sieved to 0.064 mm using a plastic sieve. Plants were purified from soil particles by washing with deionised water, dried for 7 days at room temperature and finally roots and leaves were analysed separately. The soil and plant samples were analysed using ICP-MS for trace elements.

Simple correlation analysis was used to examine the relationship between the analysed elements in soil. After reviewing several sequential extraction methods, a modification of Tessier et al method (1979) was chosen for this study as described in table 1. Eight subsoil samples were selected for sequential extraction analysis.

The sequential extraction method was carried out progressively on an initial weight of 1.0 g of soil using the following extractions: (1) exchangeable (EXCH), (2) Carbonate bound (CARB), (3) bound to Mn-Fe oxides (FeO-MnO), (4) organic matter (OM) and (5) residual (RES). After each extraction step, supernatant was first separated by centrifugation and aliquot was analysed using ICP-MS for 10 elements (Cu, Mo, Cd, Pb, Ag, As, Fe, Mn, Ni and Zn). The solid phase was added with reagents, for the next subsequent extraction.

3. Results and discussion

Average total content of some elements in two depths (0-5 cm and 15-20cm) of collected soils is shown in Table 1. Among the examined elements, contamination by Cu, Mo, Ag, Pb and As in soil was more marked than other elements. These results are derived by comparison of average concentration of elements that are far from the contaminated area (samples No 17 and No 23) and are selected as background samples. Topsoil samples (0-5cm) have higher levels of Ag, Cr, Cu, Fe, Mo, Se and Pb than subsoil samples (15-20cm) as shown in Table 1. Generally, Cu is accumulated in the upper few centimeters of soils, but it has a tendency to be adsorbed by organic compounds, carbonates, clay minerals and oxyhydroxides of Mn and Fe

also in deeper soil layers (Kabata-Pendias and Mukherjee, 2007). High levels of As (28.57 mg.kg^{-1}), Cu ($482.69 \text{ mg.kg}^{-1}$) and Ag (0.88 mg.kg^{-1}) in soil samples in comparison to unpolluted soils of background poses a potential risk in this area.

The relationship of elements to each other was evaluated by simple correlation procedures (Table 2). The strongest correlation has shown between Zn and Cd ($r = 0.90$; $p < 0.01$) and between Zn and Pb ($r = 0.82$; $p < 0.01$). The geochemical behaviors of Pb and Zn are known to be similar in most natural processes. Jalali and Khanlari (2007) reported highest correlation between Zn and Cd in soil, too. Other significant correlations were Cr and Ni ($r = 0.83$; $p < 0.01$), Mo and S ($r = 0.87$; $P < 0.01$) and between Cd and Pb ($r = 0.83$; $p < 0.01$).

The results of plant analysis are illustrated on table 3. Element concentrations in the roots and leaves differed considerably between 3 plant species. Element concentrations in Astragalus species is higher than other species (Artemisia and Acanthophyllum) Except for Pb and Cd which have highest concentration in Artemisia. Lowest concentrations are found in leaves of Acanthophyllum species for all elements. Artemisia accumulated the highest element concentrations in the leaves except for Ag, Pb and Cd. The Pb values determined in the leaves of Astragalus ranged between 0.7 - 11.3 mg/kg thus showing that there is no significant accumulation of Pb except for sample No.37 that have very high Pb concentration (511 mg/kg) relative to high Pb content of soil sample in this area (749.6 mg.kg^{-1}). Cu concentrations observed in Astragalus samples varied from 13.5 to 199.5 mg.kg^{-1} for leaves and 5.8 to 581.4 mg.kg^{-1} for roots.

The relationship between trace element concentrations in soils and vegetation can be better investigated by calculating the transfer factor (accumulation ratios) in vegetation (element concentration in vegetation/element concentration in soil) (kabata-pendias and pendias 2001). The order of decreasing median transfer factor in 3 species with little differences between the three plant species was: $\text{Cd} > \text{Mo} > \text{Cu} > \text{As} > \text{Mg} > \text{Mn} > \text{Zn} > \text{Pb} > \text{Fe} > \text{Ni} > \text{Ag} > \text{Co} > \text{Cr}$. This could be due to differing uptake behavior between the three analysed plant species.

Metal uptake by plants is extensively studied. In many studies, the exchangeable or the exchangeable plus acid soluble (Delmas et al., 2002) fractions are considered available for plant uptake. The distribution of the metals among the five fractions of Tessier's scheme is summarized in Table 4, and the results from sequential extraction are shown in Fig 2.

The hydrous oxides of Fe and Mn provide the main control on Cu fixation in soil (Davies. 1997) and Copper is known to have a high affinity for organic matter (Chlopecka. 1996) and the preference of Cu for organic matter is supported by the high stability constant of Cu complexes with organic matter (Ramos et al. 1999). The results of sequential extraction analysis show that more than 66% of Cu was extracted bound to Fe-Mn oxides fraction, followed by the Res- (22%) and OM- (9.2%) fractions. The amounts of As in the RES-, FeO-MnO, and Exch-fractions of the soil accounted for 48.6, 30.5 and 14.5% of the total As content, respectively. The highest amounts of Cd (86.65%) and Ag (40.88%) were found in the Exch-fraction. Cd content in the fist three fractions comprised about 99.6% of the total Cd because of the high extractability of Cd into Exch-fraction (86.6%).

Metal concentrations leached in Tessier's first fraction provide a conservative estimate of the level of plant available metals. So the majority of Cd in the investigated soils is in the available form for plants. The order of extractability of Cu, Co, Ni, Zn and Pb into the five fractions was: $\text{FeO-MnO} > \text{RES} > \text{OM} > \text{EXCH} > \text{CARB}$. Higher proportions of Ag are extracted

in the first state (exchangeable fraction) which is 40.8% of the total concentrations in soils. Step 2 (CARB) represents the second most significant sink for Mo after the 25% of Mo extracted into step5 (residual). The following average mobility sequence was observed: Cd > Mg > Mo > As > Cr > Pb.

4. Conclusion

Miduk soil is contaminated with Cu, Mo, Ag, Pb and As to some extent. The high concentrations of the Cd, Mg and Mo extracted in to the first three fractions show that these metals could be easily mobilized upon changes in ionic strength or a drop in pH and redox potential. Sequential extraction of soil samples indicate that bioavailability of Cd, Mg and Mo can pose a potential risk in this area. Furthermore Cd and Mo showed highest transfer factor from soil to plant.

Table. 1 Average of Total element concentrations (mg.kg⁻¹) in soil samples

Element	Ag	As	Cd	Cr	Cu	Fe	Mo	Ni	Pb	Zn
Topsoil	0.92	28.40	0.59	95.00	682.24	46321.29	6.15	51.39	133.10	227.99
Subsoil	0.84	28.75	0.61	93.86	283.14	43550.29	2.35	54.71	111.52	262.50
Background	0.21	13.275	0.37	85.75	74.97	38754.50	0.95	53.75	40.77	64.00

Table. 2 Simple correlation coefficients (r) between elements in soil (p < 0.01)

Element	Ag	As	Cd	Cr	Cu	Fe	Mg	Mo	Pb	Ni	Mn	Zn
Zn	0.47	0.04	0.90	0.43	0.06	0.18	0.12	-0.11	0.82	0.32	0.47	1.00
Mn	0.21	0.01	0.47	0.04	-0.05	0.14	0.05	-0.30	0.32	0.06	1.00	
Ni	0.12	-0.19	0.30	0.84	-0.22	0.21	0.68	-0.38	0.21	1.00		
Pb	0.54	0.17	0.84	0.36	0.22	0.27	0.18	0.07	1.00			
Mo	0.08	0.47	-0.11	-0.13	0.70	0.31	-0.43	1.00				
Mg	0.04	-0.31	0.13	0.63	-0.22	-0.04	1.00					
Fe	0.36	0.37	0.23	0.23	0.27	1.00						
Cu	0.51	0.67	0.06	-0.03	1.00							
Cr	0.27	-0.03	0.33	1.00								
Cd	0.42	0.03	1.00									
As	0.61	1.00										
Ag	1.00											

Table. 3 Mean of total element concentrations (mg.kg⁻¹) in roots and leaves of 3 plant species

AR Artemisia; AS Astragalus; AC Acanthophyllum; L Leaves; R Roots						
Element	AR_L	AR_R	AS_L	AS_R	AC_L	AC_R
Ag	0.04	0.07	0.04	0.19	0.02	0.08
Cd	0.50	0.47	1.00	0.32	0.28	0.40
Mo	1.19	0.67	1.87	2.86	0.47	1.21
Fe	2668.79	2306.33	3370.86	5835.78	877.86	4034.44
Mn	182.96	87.11	143.14	193.56	74.57	189.67
Cr	5.25	3.78	5.36	8.67	2.61	5.44
Cu	89.34	42.80	64.74	95.76	34.86	48.72
Ni	4.64	3.44	4.68	7.22	1.82	6.11
Pb	6.05	12.79	12.15	61.93	1.53	22.34
As	2.69	2.16	2.42	7.21	0.63	3.82

Table. 4 Element concentrations (mg.kg⁻¹) extracted into five fractions of Tessier's scheme

Fraction	Ag	As	Cd	Cu	Mn	Mo	Ni	Cr	Zn	Pb
EXCH	40.89	14.51	86.66	0.93	0.42	25.30	2.24	10.57	4.76	4.35
CARB	2.20	1.29	6.66	1.10	2.22	2.84	1.71	6.32	3.79	1.21
FeO-MnO	11.25	30.57	6.3	66.43	83.19	3.13	68.92	39.15	52.36	45.5
OM	26.99	4.96	0.16	9.24	3.15	20.70	5.89	13.75	10.69	5.23
RES	18.68	48.68	0.17	22.00	11.02	48.03	21.24	30.20	28.39	43.70

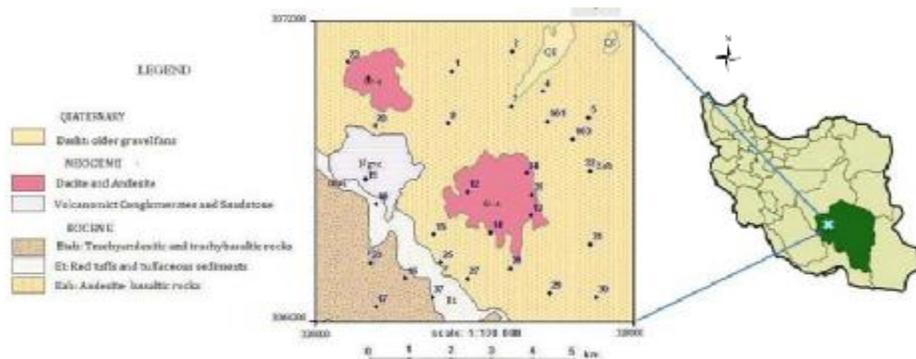


Fig. 1 geological map and stations of soil and plant sampling points

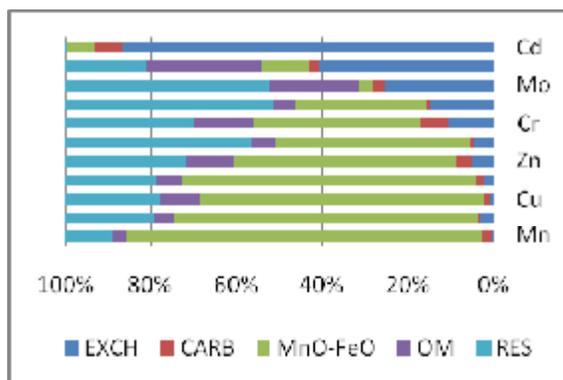


Fig. 2 Element fractionations (mg.kg⁻¹) in 8 subsoil (15-20cm) samples

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