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Determination of Sources and Distribution of Heavy Metal Pollutants in the Soil in the Area of Sarcheshmeh Copper Mine

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ABSTRACT

Existence of a tremendously huge, productive copper mine in Sarcheshmeh region and possibility of soil pollution in this area have been the main grounds behind the current investigation. In this very regard, the present study has been conducted and introduced to estimate the concentrations of cadmium (Cd), molybdenum (Mo) and lead (Pb) in the soil of Sarcheshmeh area. Soil samples were digested by EPA method; then, the obtained solution was diluted with 20 mL of water. After specifying the proportion of the sample heavy metals were determined by flame atomic absorption spectroscopy. Investigating the region's pollution maps, it was noticed that the farther the distance goes from the copper mine, the more the concentrations of the noted elements taper off. Among the three studied elements, Pb with the concentrations of 16.5 and 14.82 mg kg^{-1} had the highest amounts in the city and in the mine of Sarcheshmeh area, respectively. Cd with 2.719 and 1.829 mg kg^{-1} and Mo with 5.02 and 5.412 mg kg^{-1} comprised the next largest quantities in the city and in the mine of Sarcheshmeh zone, in respective order. The study finally suggests that with the impacts of controlling and filtering the copper mine's water wastes, the pollution of most elements in the soil could be decreased significantly.

Key words: Heavy metal, soil, pollutant, cadmium, molybdenum, lead, Sarcheshmeh copper mine

INTRODUCTION

In recent decades considerable attention has been paid to the problem of soil contamination with heavy metals to prevent further environmental determination and to examine applicable method of soil remediation.

Heavy metals in soil have been considered to be powerful tracers for monitoring the impact of human activities (Kelly *et al.*, 1996; Manta *et al.*, 2002).

An investigation on the contaminative sources of the water in Germany has shown that the amount of pollutants, especially heavy elements, in the sediments of Chechlo river has a direct link with presence or absence of industrial zones and entrance of sewages to the river. The influence of effluent sources on pollution of the bottom sediments of the small Chechlo river in southern Poland is vivid, depending on morphology of the riverbed and the hydrological conditions. Besides, the suspended particles and contaminating substances are carried even several kilometers downstream from the source of pollution until they are finally deposited in the sediment on the river's bottom (Ciszewski, 1997).

According to investigation of sediment pollution in Izmir Bay, the sediment samples were collected from 100 location, five rivers and five sewer outfalls. The collected samples analyzed by FAAS[1], FAES[2], GFAAS[3], XRF[4]. The FAAS, XRF and INAA techniques agreed fairly well for most of the elements studied. The concentration of elements showed significant differences between inner, middle and outer bays with higher concentration in the inner bay. The distribution of the crustal enrichment factor were also prepared and investigated (Atgin *et al.*, 2000).

On 25 April 1998, the pyrite mine located in Aznolcollar in Spain was collapsed. Soil pollution was studied after the spill of it between 1998 and 2001. The concentration of As, Zn, Cd, Cu and Pb are measured, the results indicated that, after three years, 50-70% of acidic soils and 25-30% of the basic soils are still highly polluted in total Arsenic. After clean-up, the homogenization of the upper 20-25 cm of the soils appeared to be the most recommended measure in the reduction of pollutions (Aguilar *et al.*, 2004).

Sample from 119 sites were collected and analyzed in 2006 in China. The average concentrations of the elements were 6.26 Mg As kg^{-1}, 52.90 mg Cr kg^{-1}, 0.066 mg Hg kg^{-1} and, 33.13 mg Pb kg^{-1}. The results of the study will assist planners and policymakers in developing effective policies to protect soil from long-term arsenic and heavy metal accumulation (Liu *et al.*, 2013).

Researcher studied to recognize the source of heavy metals in surface soils in Hamadan province in western Iran using multivariate geostatistical techniques. A total of 263 surface (0-10 cm) soil samples and 18 rock samples from major parent materials were collected cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn) contents of the samples over determined. Generally, Zn and (Pb) showed a less significant correlation with soil properties (Taghipour *et al.*, 2011).

Among the different kinds of contaminants, heavy metals are especially dangerous because of their ubiquity, toxicity and persistence (Poggio *et al.*, 2009). Some elements in this group are required by most living organisms in small but critical concentrations for their normal and healthy growth, while higher concentrations may even cause toxicity. Heavy metals differ in their chemical properties and are used widely in electronic and mechanical gadgets as well as in the artifacts of everyday life and high-tech applications. Consequently, they tend to reach the environment from a vast array of anthropogenic sources as well as from natural geochemical processes (Facchinelli *et al.*, 2001; Martin *et al.*, 2006; Zhang, 2006; Chen *et al.*, 2009).

The objective of the present was to characterize the pollution of the soils affected by copper mine of Sarcheshmeh in the catchment area.

MATERIALS AND METHODS

Statistics and primary data collecting: Collecting the statistics and all the data related to the watersheds of the upstream river ending to the sedimentary dam of Sarcheshmeh copper factory and its shallow section was done. The statistics and information of soil and water resources, hydrology, geology, lithology, waterways network, topography, physiography, exploitation of soil and water resources, also weather and climate, were regarded.

Adjustment and completion of the statistics and data related to the watersheds of the two branches of Shoor river, joining each other in the sedimentary dam of Sarcheshmeh copper factory, were done. The data of shallow section of the dam extending to Rafsanjan plain were also extracted through desert monitoring, map completing, as well as providing the descriptive basic maps and

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[1]FAAS: Flame Atomic Absorption spectroscopy, [2]FAAS: Flame Atomic emission spectroscopy, [3]GFAAS: Graphite furnace atomic absorption spectroscopy, [4]XRF: X-ray fluorescence, [5]INAA: Instrumental neutron activation analysis

basic data. All the information particularly related to weather and climate, geology, lithology, geomorphology, topography, physiography, soil survey, exploitation of land plots, hydrology, underground waters and the quality of surface and ground waters.

Preparing the basic maps to determine the sampling area: In this section of study, the work units' map is prepared according to lithology and slope map, as well as determining the homogeneous working unit through not only gathering the working map but also integrating similarities and differences of three mentioned factors in the upstream and downstream section of sedimentary dam of Sarcheshmeh factory.

Preparation of work unit: The map of work units was prepared by integrating the slope to lithology maps and then the homogeneous units were sampled in different points of studied field.

Soil sampling: A total of 168 samples were collected in 3 depth: 0-10, 10-20 and 20-40 cm including 56 samples in each depth, in work units of Sharcheshmeh area. Soil samples were obtained by mixing 5-10 sub-samples from each work unit. About 1 kg of each soil sample was collected using stainless steel spade and stored in self- sealing plastic bags. The spade was washed with deionized water and wiped dry with paper towels between each up. Geographical coordinated of sampling locations were recorded at each sampling point with a GPS[1].

Analytical procedure: All soil samples were air-dried gently ground and sieved through a 2 mm poly ethylene sieve to remove stones, coarse materials and other debris. All handling procedures were carried out without contacting any metals to avoid potential cross-contamination of samples. Then, 1 g of powdered and dried soil was transferred into a distillation flask, covered by 10 mL of concentrated HNO_3 and heated for 30 min. Then an additional 10 mL HNO_3 was added and mixture boiled under reflux. When the residue become bright, 10 mL 6N HCL was added and heating repeated. After heating, the solution was diluted with 20 mL of water, filtered in to a 50 mL volumetric flask and made up to volume.

After the proportion of sample, Cd, Pb and Mo were determined by flame atomic absorption spectroscopy (AA Seri Thermoelemental, UK).

Statistical analysis: All statistical analysis in this study was performed using MSTAT-C software by Duncan's multiple range tests at 1% level of probability. Randomized Complete Block Design (RCBD) was used in analysis of variance. Geochemical maps of heavy metals were obtained using the extraction of geostatistical analysis of geography information.

RESULTS AND DISCUSSION

Heavy metal concentrations: Concentration of Cd, Mo and Pb in soil around of Sarcheshmeh is presented in Table 1. The concentration range of Cd, Mo and Pb were 0-12.55, 2-70.5, 21-321 mg kg^{-1} in 0-10 cm depth; 0-5.00, 0.22-91.5, 3.35-333.5 mg kg^{-1} in 10-20 cm depth and 0-3.5, 3-63.5, 23.5-242 mg kg^{-1} in 20-40 cm depth, respectively. The mean value of Cd, Mo and Pb was 1.99, 13.36, 81.35 mg kg^{-1} in 0-10 cm, 1.09, 14.84, 68.02 in 10-20 cm and 1.11, 13.72, 60.25 mg kg^{-1} in 20-40 cm depth, respectively.

Mean concentration of the heavy metals in the soil of Sracheshmeh copper mine around, decreased in order of 0-10>10-20>20-40 cm depth.

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[1] Global Positioning System

Table 1: Concentration of Cd, Mo and Pb in Soil around of sarcheshmeh

Dept. (cm)	Heavy metal	Min	Max	Mean	S.D	C.V
0-10	Cd	0	12.55	1.99	1.33	0.67
10-20	Cd	0	5	1.09	8.74	0.77
20-40	Cd	0	3.5	1.11	44.07	0.71
0-10	Mo	2	70.5	13.36	0.84	0.65
10-20	Mo	0.22	91.5	14.48	10.29	0.69
20-40	Mo	3	63.5	13.72	38.08	0.64
0-10	Pb	21	321	81.35	0.79	0.54
10-20	Pb	3.35	333.5	68.02	8.78	0.56
20-.40	Pb	23.5	242	60.25	26.21	0.43

Confidence limits 99%

Table 2: Mean of square of soil samples

		Mean of squares		
Resources of variation	Degree of freedom	Cd	Mo	Pb
Replicate (sampling points)	55	0.756	3.549	16.477
Treatment (sampling depths)	2	2.10	0.446 n.s	17.34
Error	110	0.220	1.746	03.211

All elements and amounts are in 99% confidence level

Table 3: Comparison results of three depths of soil sample by Duncan's method

	Cd		Mo		Pb	
Depth (cm)	Class	Mean	Class	Mean	Class	Mean
0-10	a	1.226	a	3.334	a	8.547
10-20	b	0.856	a	3.511	b	7.652
20-40	b	0.940	a	3.446	b	7.526

Difference of means with letters mean is not significant according to Duncan's test

Statistical results: In this study, for analysis of variance, sampling points were used as replicate and sampling depths were used as treatment. Table 2 shows the mean of square of soil samples. The result of variance analysis showed that there is no significant difference between sampling points of all element in the 99% confidence level.

The comparison of the mean of sampling points in soil of working units by Duncan's method demonstrated that the points were categorized to 8 classes in terms of the Pb degree. The most amount of Pb is located both in the mine and near the city of Sarcheshmeh. Also, the concentration of Pb is high in the other parts of the mine. The more the distance becomes far away from the mine, the more Pb concentration was decreased.

The sampling spots are located in the both two classes of "a" and "b" in the terms of molybdenum (Mo). Although, the difference of concentrations is not significant for Mo, but the concentration of Mo was decreased by going away from mine.

These points categorized in 7 classes in the terms of Cd concentration. The difference of concentrations is not significant for Cd, too. The concentration of Cd is decreased by more distant from the copper mine.

The comparison results of three dept of soil sample by Duncan's method are showed in Table 3. Comparison means of three sampling depth shows that are located in two classes "a" and "b" with a view of cadmium. The highest amount of cadmium is in the depth of 0-10 cm that is located in the class "a". The depths of 10-20 and 20-40 cm are not significant with a view of cadmium. Pb has significant difference between the three depths and is located in two classes "a" and "b". The highest concentration of Pb is in the depth of 0-10 cm. There is not significant difference in 10-20 and 20-40 depths and they are located in "b" class. There is no significant difference for Mo in three depths and it is in "a" class. Therefore, concentration of Cd and Pb in 0-10 depth is more than the other depths. In distribution map of Pb is observed the maximum amount of Pb is in soil of mine, factory and Sarcheshmeh town. Its concentration decreases from mine to town. For Cd and Mo is the same. Concentration of Pb, Mo and Cd from the mine and Sarcheshmeh town to the city of Rafsanjan is reduced in depths 0-10 and 10-20 cm. Two sources contaminant were observed for Cd that probably depends on the type of soil and land. There was a trend for. The molybdenum and lead didn't follow the pattern. The concentration of Pb, Cd and Mo, were reduced from the mine and Sarcheshmeh town toward Rafsanjan. Also, the centers of contaminant were the mine of copper, factory and city of Sarcheshmeh. By comparing to results of measured with permission limit of these heavy metal in soil, we can say that the degree of Pb is in the permissible limit and Cd is higher than it. The results can be observed in Fig. 1.

The findings are clearly comparable to other studies. In northern England, the highest concentrations were detected in samples collected from near the source of pollution. There was a decrease in metal contents with increasing the distance from the pollution source (Akbar *et al.*, 2006). In Saudi Arabia, researchers indicated that all of the metals are concentrated on surface soil and decrease in the lower part of the soil (Odat and Alshammari, 2011). In Hamadan of Iran, the highest concentration of the heavy metals was recorded in top soil near Dashkason's gold mine.

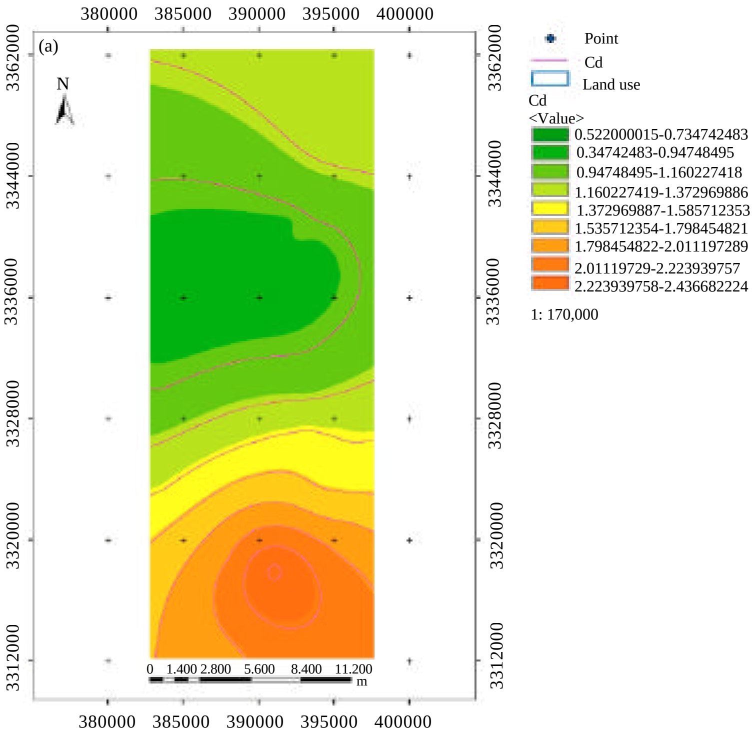

Fig. 1(a-c): Continue

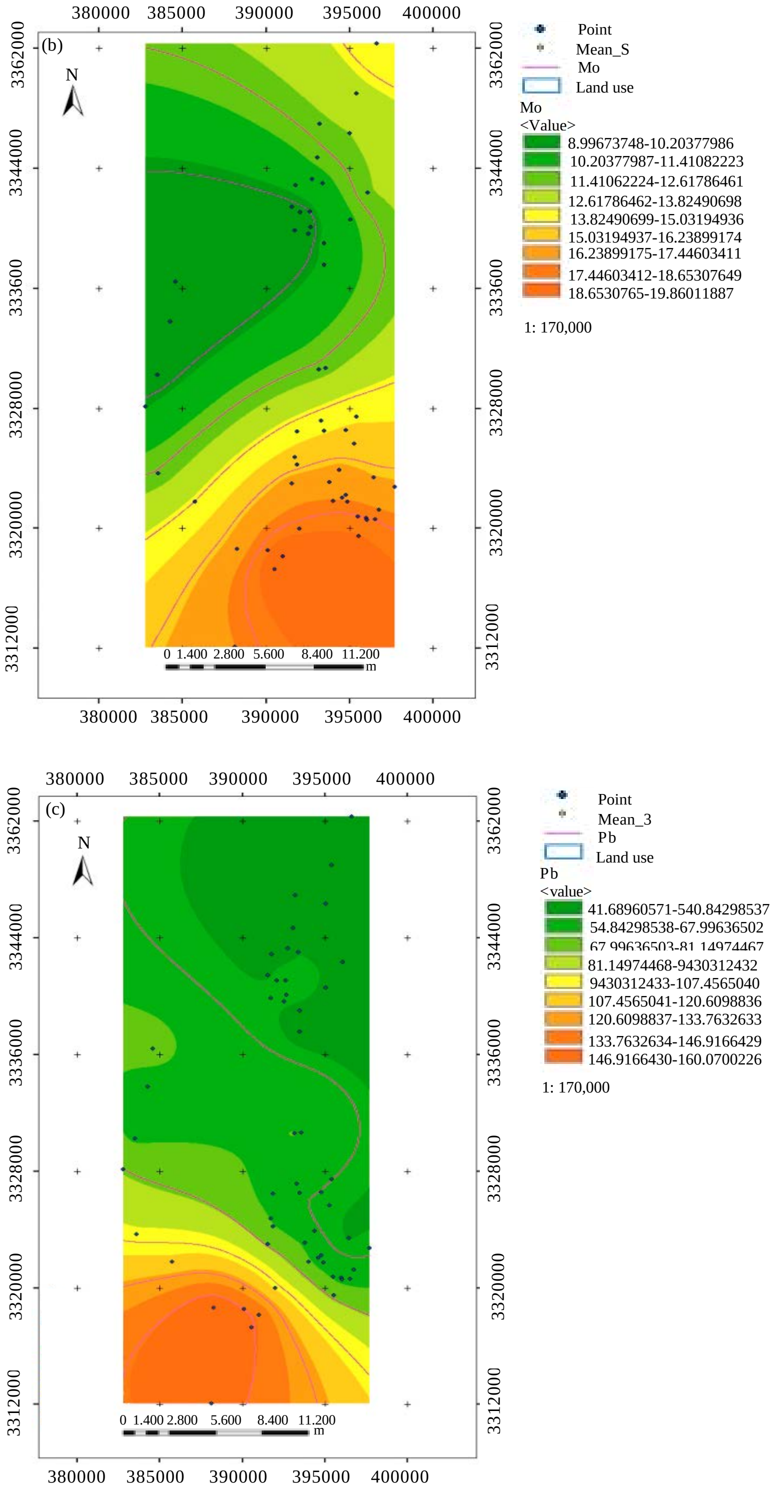

Fig. 1(a-c): Distribution maps of the studied heavy metals in soil around Sarcheshmeh copper mine (a) Cd, (b) Mo and (c) Pb dispersion in soil for mean of 3 depths

There is a progressive decrease of heavy elements' concentrations with increasing the distance from the mine (Rafiei *et al.*, 2010). At last, heavy metal contaminants of soil were detected around Imcheon gold-silver mine in Korea, as well. They also concluded that the concentration of the metals decreased exponentially with increasing the distance from the mine (Jung, 2001).

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