

Application of Various Methods for Evaluation of Heavy Metal Pollution in Soils around Agarak Copper-Molybdenum Mine Complex, Armenia

K. A. Ghazaryan, H. S. Movsesyan, N. P. Ghazaryan

Abstract—The present study was aimed in assessing the heavy metal pollution of the soils around Agarak copper-molybdenum mine complex and related environmental risks. This mine complex is located in the south-east part of Armenia, and the present study was conducted in 2013. The soils of the five riskiest sites of this region were studied: surroundings of the open mine, the sites adjacent to processing plant of Agarak copper-molybdenum mine complex, surroundings of Darazam active tailing dump, the recultivated tailing dump of “ravine - 2”, and the recultivated tailing dump of “ravine - 3”. The mountain cambisol was the main soil type in the study sites. The level of soil contamination by heavy metals was assessed by Contamination factors (*C_f*), Degree of contamination (*C_d*), Geoaccumulation index (*I-geo*) and Enrichment factor (*EF*). The distribution pattern of trace metals in the soil profile according to *C_f*, *C_d*, *I-geo* and *EF* values shows that the soil is much polluted. Almost in all studied sites, Cu, Mo, Pb, and Cd were the main polluting heavy metals, and this was conditioned by Agarak copper-molybdenum mine complex activity. It is necessary to state that the pollution problem becomes pressing as some parts of these highly polluted region are inhabited by population, and agriculture is highly developed there; therefore, heavy metals can be transferred into human bodies through food chains and have direct influence on public health. Since the induced pollution can pose serious threats to public health, further investigations on soil and vegetation pollution are recommended. Finally, *C_f* calculating based on distance from the pollution source and the wind direction can provide more reasonable results.

Keywords—Agarak copper-molybdenum mine complex, heavy metals, soil contamination, enrichment factor, Armenia.

I. INTRODUCTION

SOIL as a part of the terrestrial ecosystem plays a crucial role in elemental cycling. It has important functions as a storage, buffer, filter, and transformation compartment supporting a homeostatic interrelationship between the biotic and abiotic components [1]. Heavy metals make a significant contribution to soil as a result of human activities such as mining, smelting, electroplating, energy and fuel production, power transmission, intensive agriculture, sludge dumping, and melting operations [2]-[5]. Over the last decades, heavy metals contamination has become an extremely important subject for the scientific community due to its diverse damage functions on the environment. The adverse effects of mining activities in the environment have been addressed by many

K. A. Ghazaryan is with the Department of Ecology and Nature Protection of the Faculty of Biology of Yerevan State University, Yerevan, Armenia (e-mail: kghazaryan@ysu.am).

authors in many parts of the world [6]-[10]. Metal mining, smelting, and processing introduce heavy metals in excess of natural soil background concentration, which threaten ecosystems, surface, and ground waters, food safety, and human health [11]-[16].

As a consequence of the recent years' rapid development of mining industry, soil heavy metal pollution has become a major concern in Armenia [17], [18]. The extent and degree of heavy metal contamination around the mines vary depending on the capacity of mining activities and geochemical characteristics of the area. Trace elements contained in the residues from mining and metallurgical operations are often dispersed and included in the particulate material or in aqueous solution by wind and/or water after their disposal [19].

Because contaminants can transfer into human bodies by food chain, the contamination of soils by heavy metals may have direct influence on the possible long-term sustainability of food production in contaminated areas and as a consequence of this on public health [20], [21]. Therefore, the research of the accumulation and migration of heavy metals in the soils is currently a very important and relevant issue. The main objective of this study is the assessment of the soil pollution level of territories adjacent to open mine, processing plant and tailing dumps of Agarak copper-molybdenum mine complex by heavy metals. The total concentration of heavy metals in the soil is a useful parameter indicating contamination intensity. In addition, the degree of pollution in soil was also assessed using *C_f*, *C_d*, *I-geo* and *EF*. By this study, it was possible to obtain the baseline data regarding the accumulation of toxic metals in soils. The results will help in designing the pollution abatement strategy to control the spread of pollutants in the environment surrounded by mining activity.

II. MATERIALS AND METHODS

Agarak copper-molybdenum mine complex is situated in the south-east of Armenia (Syunik Marz). The soils of the five riskiest sites of this region were studied:

- surroundings of the open mine (samples № 1-5),
- the sites adjacent to processing plant of Agarak copper-molybdenum mine complex (samples № 6-7),
- surroundings of Darazam active tailing dump (sample № 8),
- recultivated tailing dump of “ravine - 2” (sample № 9),
- recultivated tailing dump of “ravine - 3” (sample № 10).

The main soil type in study sites is the mountain cambisol with its two subtypes: the typical mountain cambisol (samples № 1-5) and the carbonate mountain cambisol (samples № 6-10 and the control sample). In Armenia, this soil type is distributed 500-1700 meters above the sea level, and on arid southern slopes it reaches up to 2400 meters [22].

The typical mountain cambisol occupied intermediate position between the carbonate and decalcified subtypes by its geographical location, morphological and physicochemical characteristics. This type of soil, compared to the carbonate type, occupied higher position above the sea level (1100-1300 meters), the gradient was 0-35 degrees, the microrelief was smooth. The soil of this subtype was not fertile and useful for agricultural purposes, except the samples № 4 and № 5. The carbonate mountain cambisol subtype of soil was distributed 700-1000 meters above the sea level, on the gradients of 0-30 degrees, the microrelief was mainly smooth. This soil was mainly very rocky; carbonates were distributed from top to bottom. This subtype of soil was not fertile and useful for agricultural purposes, except the № 7 and control samples.

For the study purpose, 10 sampling sites were selected in 2013. The control section was done in the site which was 2 km away from the processing plant in the direction of Agarak town (at a distance of 550 km from motor road). The coordinates of sampling sites were recorded by GPS.

The sampling of soils was carried out in a traditional way, well-known in soil science. All labware and sampling apparatus were pre-soaked in 5% nitric acid solution followed by distilled water for a day prior to sampling for removing the trace concentrations of metals.

The samples of soils were taken from a depth of 0-20 cm at 5 m intervals on a grid measuring 20 m x 20 m and with the center point of the grid at the sample location. The sections were done manually. All samples were collected into polyethylene sampling bottles and transported to the laboratory. After homogenization and removal of unwanted content (stones, plant material, etc.), the samples were air-dried at room temperature, sieved to pass a 1 mm mesh and stored in an all-glass jar for analysis of their properties.

Before analysis, the samples need required digestion. Soil was grounded in a mortar and pestle to pass a 0.42 mm nylon mesh. Total concentration of heavy metals was determined using Aqua Regia (HCl-HNO₃, 3:1) extraction method (3g of soil sample were digested for 2h at 180°C). Heavy metals were determined by atomic absorption spectrometry method (AAS) using Atomic-absorption spectrometer PG990 (PG Instruments LTD).

The level of soil contamination by heavy metals was assessed by contamination indices. *Cf*, *Cd*, *I-geo*, and *EF* were used.

Cf and *Cd* were calculated as suggested by Håkanson [23] through following formulas:

$$Cf^i = Cs^i / Cb^i \quad (1)$$

$$Cd = \sum Cf \quad (2)$$

where, Cs^i is the measured concentration of the examined metal i in the soil sample, and Cb^i is the background value of heavy metal i in the uncontaminated soil (control). Håkanson suggested four classes of *Cf* to evaluate the metal contamination levels as shown in Table I [23]. Four categories of *Cd* as suggested were used to evaluate metal contamination levels (Table I). If the *Cd* value exceeds 20, then it is necessary to take the immediate counter measures to reduce the heavy metal contamination in the soil.

I-geo was used to calculate metal contamination level in the soils. *I-geo* was originally defined by Müller, in order to determine and define metal contamination in sediments, by comparing the current concentrations with pre-industrial levels. The index is calculated as [24]:

$$I-geo = \log_2 Cs^i / 1.5 Cb^i \quad (3)$$

where Cs^i is the concentration of the element i in the samples, Cb^i is the background value of the element i , and the factor 1.5 is used to take into account the possible lithological variability. The rank of values of *I-geo* and its implication is shown in Table I.

TABLE I
 DIFFERENT TYPES OF MODEL AND THE CATEGORIES FOR THE DESCRIPTION OF SOIL CONTAMINATION

Model	Class	Description	Sources
<i>Cf</i>	$Cf \leq 1$	Low	[23]
	$1 < Cf \leq 3$	Moderate	
	$3 < Cf \leq 6$	Considerable	
	$6 < Cf$	Very high	
<i>Cd</i>	$Cd \leq 11$	Low	[23]
	$11 < Cd \leq 22$	Moderate	
	$22 < Cd \leq 33$	Considerable	
	$33 < Cd$	Very high	
Geoaccumulation index	$I-geo \leq 0$	Uncontaminated	[24]
	$0 < I-geo \leq 1$	Uncontaminated to moderately contaminated	
	$1 < I-geo \leq 2$	Moderately contaminated	
	$2 < I-geo \leq 3$	Moderately to strongly contaminated	
	$3 < I-geo \leq 4$	Strongly contaminated	
	$4 < I-geo \leq 5$	Strongly to very strongly contaminated	
	$5 < I-geo$	Very strongly contaminated	
	$EF \leq 2$	Depletion to minimal enrichment suggestive for or minimal pollution	
<i>EF</i>	$2 < EF \leq 5$	Moderate enrichment, suggestive of moderate pollution	[25]
	$5 < EF \leq 20$	Significant enrichment, suggestive of a significant pollution signal	
	$20 < EF \leq 40$	Very highly enriched, indicating a very strong pollution signal	
	$EF > 40$	Extremely enriched, indicating an extreme pollution signal	

The value of *EF* was calculated using the modified formula given [25] based on the equation suggested by [26]. The *EF* was based on the standardization of a tested element against a reference one. A reference element is characterized by the low occurrence variability [27]. In this study, aluminium (Al) was

used as reference since it belongs to the lithophile elements, and it has a high chemical stability during weathering. The EF is calculated according to:

$$EF = \frac{(C_n/C_{ref})}{(B_n/B_{ref})} \quad (4)$$

where, C_n is the concentration of n element in soil, C_{ref} is the content of the reference element in the examined environment, B_n is the content of examined n element in the reference environment and B_{ref} is the content of the reference element in the reference environment.

Analysis of variance was used to compare the mean metal concentrations among the sites. Further evaluation was done via Duncan's multiple range tests. The statistical analysis was performed by using SPSS software, version 15.

III. RESULTS AND DISCUSSION

The concentrations of V, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Pb and Cd in the soils adjacent to open mine near Agarak copper-molybdenum mine complex were determined, and the degree of heavy metal pollution in the soils was assessed. The ranges of mean concentration (mg/kg) of heavy metals in 5 study areas are as following: V (8.2 – 16.3), Cr (0.6 – 6.8), Mn (39.2-184.5), Co (1.2-2.1), Ni (0.7-4.1), Cu (17.4-145.5), Zn (4.4-19.2), As (0.4-1.6), Mo (0.6-13.2), Pb (0.6-6.4) and Cd (0.01-0.22) (Table II). Since the contents of metals in soils are specific and depend on the compound of rocks producing soil and the conditions of soil formation, for determination of pollution level, the obtained results were compared to the control sample which was considered as a background.

TABLE II
 THE MEAN CONCENTRATIONS (MG/KG) OF SOME HEAVY METALS IN THE STUDIED SAMPLES OF SOIL

Sample number	V	Cr	Mn	Co	Ni	Cu	Zn	As	Mo	Pb	Cd
1	12.5±3.4	1.4±0.4	54.3±14.9	2.1±0.4	1.3±0.4	53.3±18.0	4.9±1.8	0.6±0.2	5.2±1.7	1.1±0.3	0.03±0.01
2	16.3±4.6	0.6±0.2	61.5±21.1	1.6±0.3	2.3±0.7	145.5±35.8	10.4±3.7	1.5±0.4	13.2±3.8	2.3±0.7	0.06±0.02
3	11.9±2.9	0.7±0.2	32.3±9.1	1.3±0.3	0.7±0.2	123.5±36.1	7.1±2.1	1.0±0.3	8.5±3.0	3.9±0.9	0.04±0.001
4	14.1±5.1	3.8±1.1	99.9±24.5	2.1±0.5	4.1±1.1	23.4±6.0	11.7±2.0	0.8±0.3	1.2±0.4	1.5±0.4	0.05±0.002
5	7.5±1.8	2.7±0.9	70.0±19.2	1.3±0.2	2.2±0.6	25.3±5.4	7.7±2.2	0.4±0.1	1.5±0.4	1.7±0.4	0.03±0.01
6	11.2±3.1	2.0±0.7	184.5±34.9	1.6±0.4	1.7±0.4	56.2±16.9	19.2±5.4	1.6±0.5	4.2±1.5	6.4±1.9	0.22±0.07
7	8.9±2.2	1.3±0.4	113.0±35.1	1.4±0.4	1.0±0.3	81.2±24.4	10.8±3.8	1.0±0.4	6.2±2.0	3.5±1.4	0.04±0.01
8	9.5±3.0	6.8±2.1	50.9±11.2	1.6±0.5	4.1±1.3	35.4±13.1	6.6±1.9	0.8±0.2	1.2±0.3	1.2±0.4	0.04±0.01
9	9.2±2.8	6.0±1.6	49.0±12.4	1.4±0.3	3.7±0.9	39.7±11.7	6.5±2.3	0.9±0.2	0.9±0.2	1.4±0.4	0.05±0.02
10	8.2±3.1	2.8±0.5	39.2±9.5	1.2±0.3	1.7±0.5	17.4±4.9	4.4±1.4	0.7±0.3	0.6±0.2	0.6±0.2	0.01±0.004
Control	7.5±1.4	2.6±0.7	56.4±13.1	1.3±0.4	2.0±0.7	9.5±3.6	8.0±1.7	0.6±0.2	0.5±0.2	0.8±0.3	0.02±0.007

TABLE III
 CORRELATION MATRIX

	V	Cr	Mn	Co	Ni	Cu	Zn	As	Mo	Pb	Cd
V	1										
Cr	-0,35	1									
Mn	0,11	-0,16	1								
Co	0,65	0,03	0,24	1							
Ni	0,08	0,85	-0,06	0,32	1						
Cu	0,64	-0,59	-0,03	-0,01	-0,41	1					
Zn	0,29	-0,22	0,93	0,19	-0,02	0,17	1				
As	0,56	-0,29	0,55	0,06	-0,11	0,65	0,72	1			
Mo	0,70	-0,70	0,02	0,09	-0,46	0,97	0,20	0,63	1		
Pb	0,21	-0,41	0,75	-0,05	-0,41	0,47	0,81	0,75	0,42	1	
Cd	0,24	-0,11	0,85	0,16	-0,05	0,15	0,89	0,75	0,15	0,84	1

A. Correlation Analysis

This is a bivariate method which represents the degree of relationship among two random variables. Interpretation of correlation gives an idea of quick soil quality monitoring method. For this purpose, Spearman's rank coefficient of correlation between the nine parameters of soil quality, namely V, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Pb and Cd was calculated for the correlation analysis as displayed in Table III. The correlation analysis will allow ascertaining if the changes of heavy metal contents in soils from different sites have a similar tendency or not. Moreover, the strong positive correlation could indicate the probability of integrated source of pollution.

The correlation coefficient of Spearman's rank is expressed by ρ , the value of which is continuously from -1.0 to +1.0. A positive ρ matches to an increasing monotonic trend between concentrations of two heavy metals whereas a negative ρ matches to a decreasing monotonic trend among concentrations of two heavy metals. The strong positive correlation ($\rho > 0.7$) was observed between Cu and Mo; Cr and Ni; Mn, Zn, Pb and Cd; As, Zn, Pb and Cd. In particular, the highest positive correlation was observed between Cu and Mo, which is a sign of occurrence of the integrated source of pollution and is conditioned by high content of mentioned heavy metals in ore. But in general, the similar tendency of above-said heavy metals to rise may be partly connected with geochemical factors.

B. Contamination Evaluation Based on Cf

Fig. 1 illustrates the calculated C_f for the measured heavy metals in soil samples. It was found during the studies that almost in all soil samples Cu, Mo, Pb and Cd are the main polluting heavy metals. Particularly, in case of Cu the maximum value of C_f was 15.32, in case of Mo – 26.4, for Pb – 8.0 and for Cd – 11.0. All these values correspond to the very high level of contamination. Such pollution of soils is directly conditioned by high content of above-mentioned heavy metals in ore processed in Agarak copper-molybdenum mine complex. The average C_f for the observed metals were in the decreasing order of Mo (9.36) > Cu (6.82) > Pb (3.19) > Cd

(3.11) >As (1.59) > V (1.5) >Mn (1.41) > Co (1.230) > Zn (1.18) > Ni (1.17) > Cr (1.08).

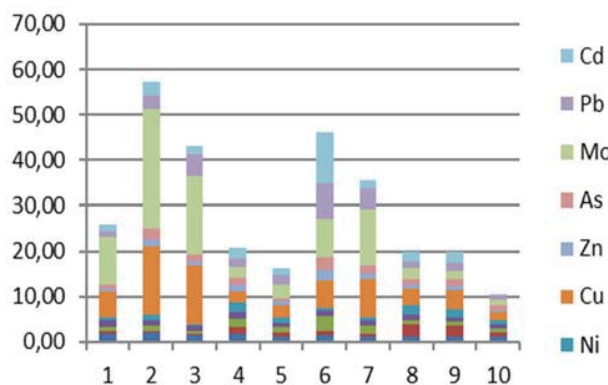


Fig. 1 Values of *C_f* of different metals in surrounding territories of Agarak copper-molybdenum mine complex

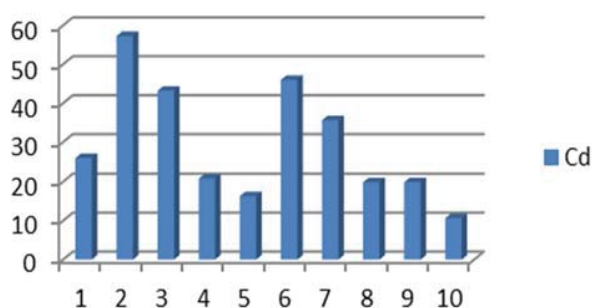


Fig. 2 *C_d* of surrounding territories of Agarak copper-molybdenum mine complex

C. Contamination Evaluation Based on *C_d*

The values of the *C_d* are presented in Fig. 2. By *C_d* value reduction the 10 investigated soil samples made the following series: 2>6>3>7>1>4>9>8>5>10. By the *C_d* value, the 10% of soil samples fall in the low level of contamination ($Cd \leq 11$), 40% of soil samples fall in the moderate level of contamination ($11 < Cd \leq 22$), 10% in the considerable level of contamination ($22 < Cd \leq 33$), 40% of soil samples fall in the very high level of contamination ($33 < Cd$).

D. Contamination Evaluation Based on *I-Geo*

I-geo was used to calculate the metal contamination level in the soils (Table V). *I-geo* values for V show that 60% of the samples fall in the uncontaminated class (≤ 0) and 40% in the uncontaminated–moderately contaminated class (0-1). *I-geo* values for Cr show that 80% of the samples fall in the uncontaminated class (≤ 0) and 20% in the uncontaminated–moderately contaminated class (0-1), for Mn show that 70% of the samples fall in the uncontaminated class (≤ 0), 20% in the uncontaminated–moderately contaminated class (0-1) and 10% are moderately contaminated (1-2), for Co show that 80% of the samples fall in the uncontaminated class (≤ 0) and 20% in the uncontaminated–moderately contaminated class (0-1), for Ni show that 70% of the samples fall in the uncontaminated class (≤ 0) and 30% in the uncontaminated–

moderately contaminated class (0-1), for Cu show that 30% in the uncontaminated–moderately contaminated class (0-1), 40% are moderately contaminated (1-2), 10% are moderately to strongly contaminated (2-3) and 20% are strongly contaminated (3-4), for Zn show that 90% of the samples fall in the uncontaminated class (≤ 0) and 10% in the uncontaminated–moderately contaminated class (0-1), for As show that 60% of the samples fall in the uncontaminated class (≤ 0) and 40% in the uncontaminated–moderately contaminated class (0-1), for Mo show that 10% of the samples fall in the uncontaminated class (≤ 0), 40% in the uncontaminated–moderately contaminated class (0-1), 20% are moderately to strongly contaminated (2-3), 20% are strongly contaminated (3-4) and 10% are strongly to very strongly contaminated (4-5), for Pb show that 30% of the samples fall in the uncontaminated class (≤ 0), 40% in the uncontaminated–moderately contaminated class (0-1), 20% are moderately contaminated (1-2) and 10% are moderately to strongly contaminated (2-3), for Cd show that 30% of the samples fall in the uncontaminated class (≤ 0), 60% in the uncontaminated–moderately contaminated class (0-1) and 10% are moderately to strongly contaminated (2-3). The average *I-geo* for the observed metals were in the decreasing order of Mo (1.83) > Cu (1.75) > Pb (0.65) > Cd (0.50) > As (-0.06) > V (-0.08) > Co (-0.35) > Mn (-0.36) > Zn (-0.56) > Ni (-0.62) > Cr (-0.88).

E. Contamination Evaluation Based on *EF*

A common approach to estimating the anthropogenic impact on soils is to calculate a normalized *EF* for metal concentrations above the uncontaminated background levels. The *EF* calculation seeks to reduce the metal variability associated with the variations in the mud/sand ratios, and is a convenient tool for plotting the geochemical trends across large geographic areas, which may have substantial variations in the mud (i.e. clay rich) to sand ratios. It was found during studies that in all soil samples the 70% of *EF* values for 11 heavy metals were less than 2 which were characterized as minimal pollution level, 21% of *EF* values corresponded to moderate pollution level, 9% - to significant pollution level. The highest *EF* values were observed in case of Cu, Mo, Pb and Cd and this once again confirms that the metals cited above are the main pollutants of soils in the studied region.

TABLE IV
THE DEGREE OF HEAVY METAL POLLUTION OF THE SOIL SAMPLES ACCORDING TO *I-GEO*

Sample number	V	Cr	Mn	Co	Ni	Cu	Zn	As	Mo	Pb	Cd
1	0.15	-1.48	-0.64	0.11	-1.21	1.90	-1.29	-0.58	2.79	-0.13	0.00
2	0.53	-2.70	-0.46	-0.29	-0.38	3.35	-0.21	0.74	4.14	0.94	1.00
3	0.08	-2.48	-1.39	-0.58	-2.10	3.12	-0.76	0.15	3.50	1.70	0.42
4	0.33	-0.04	0.24	0.11	0.45	0.72	-0.04	-0.17	0.68	0.32	0.74
5	-0.58	-0.53	-0.27	-0.58	-0.45	0.83	-0.64	-1.17	1.00	0.50	0.00
6	-0.01	-0.96	1.12	-0.29	-0.82	1.98	0.68	0.83	2.49	2.42	2.87
7	-0.34	-1.58	0.42	-0.48	-1.58	2.51	-0.15	0.15	3.05	1.54	0.42
8	-0.24	0.80	-0.73	-0.29	0.45	1.31	-0.86	-0.17	0.68	0.00	0.42
9	-0.29	0.62	-0.79	-0.48	0.30	1.48	-0.88	0.00	0.26	0.22	0.74
10	-0.46	-0.48	-1.11	-0.70	-0.82	0.29	-1.45	-0.36	-0.32	-1.00	-1.58

TABLE V
THE DEGREE OF HEAVY METAL POLLUTION OF THE SOIL SAMPLES ACCORDING TO *EF*

Sample number	V	Cr	Mn	Co	Ni	Cu	Zn	As	Mo	Pb	Cd
1	1.39	0.45	0.80	1.34	0.54	4.67	0.51	0.83	8.65	1.14	1.25
2	1.31	0.14	0.65	0.74	0.69	9.20	0.78	1.50	15.85	1.73	1.80
3	1.28	0.22	0.46	0.81	0.28	10.48	0.72	1.34	13.70	3.93	1.61
4	1.85	1.43	1.74	1.59	2.01	2.42	1.44	1.31	2.36	1.84	2.45
5	0.92	0.96	1.14	0.92	1.01	2.45	0.89	0.61	2.76	1.96	1.38
6	1.17	0.60	2.57	0.97	0.67	4.64	1.88	2.09	6.59	6.28	8.63
7	1.01	0.43	1.71	0.92	0.43	7.9	1.15	1.42	10.58	3.73	1.71
8	1.30	2.68	0.93	1.26	2.10	3.82	0.85	1.37	2.46	1.54	2.05
9	1.39	2.61	0.98	1.22	2.09	4.73	0.92	1.70	2.04	1.98	2.83
10	1.29	1.28	0.82	1.09	1.01	2.17	0.65	1.38	1.42	0.89	0.59

IV. CONCLUSION

The assessment of heavy metal contamination (V, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Pb and Cd) in soils from selected sites in surroundings of Agarak copper-molybdenum mine complex (open mine, processing plant, one active and two recultivated tailing dumps) was made in comparison with the control site. The strong positive correlation was observed between some heavy metals in the studied area. The highest positive correlation was observed between Cu and Mo, which is a sign of occurrence of the integrated source of pollution and is conditioned by the high content of mentioned heavy metals in ore. The distribution pattern of trace metals in the soil profile according to *Cf*, *Cd*, *I-geo* and *EF* values shows that the soil is much polluted. Almost in all studied sites Cu, Mo, Pb and Cd were the main polluting heavy metals. According to *EF* values the pollution by mentioned metals has been evaluated in some soil samples as "significant pollution". The high values of *Cd* in soil samples № 2 and № 3 (57.27 and 43.21, respectively) collected from the surroundings of open mine are conditioned by peculiarities of relief, in particular by comparatively low location above the sea level and by direction of winds. The high value of *Cd* in № 6 soil sample is connected with the operation of ore grinding mill in the vicinity of this point. From three tailing dumps, the maximum value of *Cd* was observed in Darazam active tailing dump, which is the operating tailing dump; therefore, the contamination level is comparatively higher there.

Taking into consideration all above-mentioned, it is essential to implement the continuous monitoring of soils in surroundings of Agarak copper-molybdenum mine complex

and to devise the methods of soil quality enhancement. This issue is very important for the conservation of the ecological balance in this territory as well as from the point of view of preserving public health because heavy metals can enter human body through soil-plant-human or soil-plant-animal-human chains and cause various diseases.

ACKNOWLEDGMENT

This work was supported by the State Committee of Science MES RA, in the frames of research project № 15T-4C251.

REFERENCES

- [1] A. Kabata-Pendias, W. Sadurski, "Trace elements and compounds in soil". In: Merian E., Anke M., Ichnat M., Stoeppler M. (eds) Elements and their compounds in the environment. Occurrence, analysis and biological relevance, v. 1: General aspects. Wiley-VCH Verlag GmbH & Co. Kga A, Weinheim, p. 79, 2004.
- [2] A.K. Krishna, P.K. Govil, "Heavy metal contamination of soil around Pali Industrial Area, Rajasthan, India", *Environ. Geol.*, v. 47, pp. 38-44, 2004.
- [3] X.S. Wang, Y. Qin, "Accumulation and sources of heavy metals in urban topsoils: a case study from the city of Xuzhou, China", *Environ. Geol.*, v. 48, pp. 101-107, 2005.
- [4] M.S. Li, Y.P. Luo, Z.Y. Su, "Heavy metal concentrations in soils and plant accumulation in a restored manganese mineland in Guangxi, South China", *Environ. Pollution*, v. 147, pp. 168-175, 2007.
- [5] M.R. Samarghandi, J. Nouri, A.R. Mesdaghinia, A.H. Mahvi, S. Nasser, F. Vaezi, "Efficiency removal of phenol, lead and cadmium by means of UV/TiO₂/H₂O₂ processes", *Int. J. Environ. Sci. Tech.*, v. 4 (1), pp. 19-25, 2007.
- [6] C.H. Lee, "Assessment of contamination load on water, soil and sediment affected by the Kongjujeil mine drainage, Republic of Korea" *Environ. Geol.*, v. 44, pp. 501-515, 2003.
- [7] A. Navarro, D. Collado, M. Carbonell, J.A. Sanchez, "Impact of mining activities on soils in a semi-arid environment: Sierra Almagrera district, SE Spain", *Environ. Geochem. Health*, v. 26, pp. 383-393, 2004.

- [8] M.E.P. Gomes, P.J.C. Favas, "Mineralogical controls on mine drainage of the abandoned Ervedosa tin mine in north-eastern Portugal", *Applied Geochemistry*, v. 21, pp. 1322–1334, 2006.
- [9] Y. Sun, Z. Xie, J. Li, J. Xu, Z. Chen, R. Naidu, "Assessment of toxicity of heavy metal contaminated soils by the toxicity characteristic leaching procedure". *Environ. Geochem. Health*, v. 28, pp. 73–78, 2006.
- [10] T. Moreno, A. Oldroyd, I. McDonald, W. Gibbons, "Preferential fractionation of trace metals-metalloids into PM 10 resuspended from contaminated gold mine tailings at Rodalquilar, Spain", *Water, Air and Soil Pollution*, v. 179, pp. 93–105, 2007.
- [11] S. Dudka, D.C. Adriano, "Environmental impacts of metal ore mining and processing: a review". *J Environ. Qual.*, v. 26, pp. 590–602, 1997.
- [12] H.M. Selim, D.L. Sparks, "Heavy metals release in soils", CRC Press LLC, Boca Raton, pp. 265, 2001.
- [13] E. Callender, Heavy metals in the environment - historical trends, In: Lollar B.S., (ed) *Treatise on Geochemistry, Environmental Geochemistry*, US Geological Survey, Westerville, RI, USA, pp. 67–105, 2004.
- [14] A.K. Krishna, P.K. Govil, "Heavy metal distribution and contamination in soils of Thane Belapur industrial development area, Mumbai, Western India", *Environ. Geol.*, v. 47, pp. 1054–1061, 2005.
- [15] O. Selinus, B. Alloway, J.A. Centeno, R.B. Finkelman, R. Fuge, U. Lindh, P. Smelday, *Essentials of medical geology: impacts of the natural environment on public health*. Elsevier Academic Press, Amsterdam, p. 793, 2005.
- [16] A.G. Kachenko, B. Singh, "Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia". *Water, Air and Soil Pollution*, v. 169, pp.101–123, 2006.
- [17] K.A. Ghazaryan, G.A. Gevorgyan, H.S. Movsesyan, N.P. Ghazaryan, K.V. Grigoryan, "The evaluation of heavy metal pollution degree in the soils around the Zangezur Copper and Molybdenum Combine", *International Journal of Environmental, Chemical, Ecological, Geological and Geophysical Engineering*, v. 9 (5), pp. 11-16, 2015.
- [18] K.A. Ghazaryan, H.S. Movsesyan, N.P. Ghazaryan, G.A. Gevorgyan, K.V. Grigoryan, Soil pollution level of ecologically vulnerable areas around Kajaran town and ways of their improvement. *Chem. J. of Moldova. General, Industrial and Ecological Chemistry*, v. 9 (2), pp. 52-57, 2014.
- [19] B.G. Lottermoser, *Mine wastes. Characterization, treatment, environmental impacts*, 2nd edn. Springer, Berlin, 2007.
- [20] T.B. Chen, J.W. Wong, H.Y. Zhou, M.H. Wong, "Assessment of trace metal distribution and contamination in surface soils of Hong Kong", *Environ. Pollut.*, v. 96 (1), pp.61–68, 1997.
- [21] B.A. Zarcinas, C.H. Ishak, M.J. McLaughlin, G. Conzens, "Heavy metals in soils and crops in southeast Asia. 1. Peninsular Malaysia", *Environ. Geochem. Health*, v. 26, pp. 343–357, 2004.
- [22] R.A. Edilyan, *Atlas of soils of the Republic of Armenia*. Yerevan, 70 p, 1990. (in Russian).
- [23] L. Håkanson, "An ecological risk index for aquatic pollution control - a sedimentological approach", *Water Research*, v. 14, pp. 975–1001, 1980.
- [24] G. Muller, "Index of geoaccumulation in sediments of the Rhine River". *Geol. J.*, v. 2 (3), pp. 108–118, 1969.
- [25] L. Krzysztof, D. Wiechula, I. Kornis, "Metal contamination of farming soils affected by industry", *Environ. Int.*, v. 30, pp. 159–165, 2003.
- [26] P. Buat-Menard, R. Chersalet, "Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter", *Earth Planet. Sci. Lett.*, v. 42, pp. 398–411, 1979.
- [27] C. Reimann, P. De Caritat, "Intrinsic flaws of element enrichment factors (EF's) in environmental geochemistry", *Environ. Sci. Technol.*, v. 34, pp. 5084–5091, 2000.